A STUDY OF THE METHODS OF CHARACTERIZATION OF INORGANIC ION EXCHANGERS AND THEIR NOVEL APPLICATIONS

A COMPILATION OF RESEARCH PAPERS SUBMITTED TO
THE ALIGARH MUSLIM UNIVERSITY ALIGARH
FOR THE AWARD OF THE DEGREE OF

Doctor of Science

IN

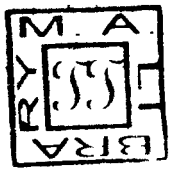
CHEMISTRY

BY

DR. KRISHNA GOPAL VARSHNEY

DEPARTMENT OF APPLIED CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

1990



Phone : Office : 6042

DEPARTMENT OF APPLIED CHEMISTRY

ZAKIR HUSAIN
COLLEGE OF ENGG. & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH—202002 (INDIA)

Ref. No.....

Dated.....July 12, 1990

CERTIFICATE

It is certified that the major portion of the work embodied in the D.Sc. Thesis entitled, "A Study of the Methods of Characterization of Inorganic Ion Exchangers and their novel Applications" is the original contribution of the candidate, Dr. A.G. Varshney, who has published total 100 research papers, out of which, 2 have been published as single author, 73 as a senior author and 24 as a junior author.

(Prof. K.T. Nasim)
CHAIRMAN

CHAIRMAN
Department of Applied Chemistry
Z. H. College of Engg & Technology
A.M.U., ALIGARH

DEDICATED

TO

MY PARENTS

AND

NIRMAL

C O N T E N T S

CHAPTER-3

KINETICS OF EXCHANGE ON SOME SYNTHETIC INORGANIC ION EXCHANGERS

ACKNOWLEDGEMENTS

The author expresses his most sincere gratitude to all his respected teachers during his post graduation and doctorate courses specially Professor A.R.Kidwai and Professor Mohsin Qureshi who always remained a real source of inspiration. During his visit to the University of Rome, Italy as a Post Doctoral Fellow the author was highly impressed by Professor Aldo LaGinestra, Professor G.Alberti and Professor U.Costantino by their all time help and useful discussions which provided him the most needed encouragement for higher studies.

The author acknowledges with thanks the full affection and timely guidance from his senior colleagues Professor A.U.Malik, Professor K.T.Nasim, Professor M.Ajmal and Professor K.M.Shamsuddin, apart from the best possible help from his other colleagues. He is also thankful to his friends Professor S.Z.Qureshi and Dr. J.P.Rawat for their useful academic discussions and suggestions. He will be failing in his duties if he overlooks the hard work put up by his excellent research team during the last span of 20 years.

The author also wishes to express his thanks to the technical, clerical and other non teaching staff of the Department for their full cooperation which made the task easier. Special thanks are due to Mr.Zainuddin for his useful suggestions. Mr. H.C.Saxena, typist, is thanked for his excellent typing skills.

Finally, the author is highly indebted to his family members and relatives who always encouraged and gave full moral support to him in his academic persuits and remained by his side at the time of distress. His mother, wife and children deserve a special appreciation for the sacrifice of their emotional sentiments as the author could not have shared many a pleasant moments with them because of his awefully busy and abnormal work schedules.

/ K.G.VARSHNEY /

PREFACE

Analytical chemistry is the science of chemical characterization and measurement. With the tremendous advancement in technology taken place the most important requirement faced by the analytical chemists at present is to achieve separations of the highest order so that the materials of the greatest purity may be obtained. It is not generally possible by the classical methods of analysis which are highly time consuming. Now-a-days the instrumental methods involve the use of the most sophisticated instruments which are sometimes out of reach for a common researcher particularly in a developing country like ours. Therefore, an emphasis is always given in the Indian research programmes for the development of methods and techniques which are simple but sufficiently accurate.

Out of the modern methods of analysis Chromatography is still one of the most versatile analytical techniques effective for the separation of complex mixtures and for the qualitative or quantitative analysis of the separated substances. Out of the two major types of chromatography (Liquid and Gas), liquid chromatography is easier to practise in ordinary chemical laboratories. If the stationary phase is solid the process is termed as "liquid adsorption chromatography". If it is an ion exchange material, either organic or inorganic, it is known as "ion exchange chromatography". In case when a liquid supported on an inert solid is taken as the stationary phase, the technique is known as partition chromatography. Again, the mobile phase may be a liquid (Liquid-liquid partition chromatography) or a gas (gas-liquid partition chromatography). Paper chromatography is a type of partition chromatography in which the stationary phase is a layer of water adsorbed on a sheet of paper. This and thin layer chromatography together are termed as "Planar chromatography".

Ion exchange chromatography, although observed in the middle of the nineteenth century, got its recognition in the

applied field only after approximately 100 years. It was so much unpopular upto 1948 that in a symposium of the New York Academy of Sciences in that year a paper on ion exchange was added only after a meeting of the editors. However, its significance was rapidly recognized and a year later in a similar symposium about half of the total number of papers dealt with it. Today, ion exchange appears to have become a dominant field of chromatography and is an important tool for research and analysis.

Although organic resins have, until recently, dominated the field, their use is limited under the conditions of high temperatures and strong radiations. Thus, an interest in inorganic materials as ion exchangers was revived. It is now more than 30 years when reports of ion exchange behaviour of zirconium phosphate gels first appeared in the literature. At present these materials have a significant position in the field of ion-exchange chromatography, owing to the fact that they are resistant to heat and radiation. They can be used for the high temperature separations of ionic components in radioactive wastes, as solid electrolytes and as catalysts.

In view of this an effort has been made here to highlight the advances made in the field of inorganic ion exchangers, with a particular reference to their synthesis, characterization and analytical applications. This thesis, which is in the form of compilation of the recently published papers by the author (and coworkers), is an attempt in that direction and mainly deals with the studies of the model systems. Fifty papers have been selected by the author out of the total 100 papers published by him so far, out of which 2 have been published as a single author, 7 as a senior author and 24 as a junior author. Following are the main fields of study:

1. Synthesis and characterization of some new inorganic ion exchangers which are stable chemically and thermally and are selective for certain metal ions, important from the pollution point of view.

2. Analytical applications of inorganic ion exchangers which include both the routine (laboratory) separations on columns, papers and thin layer of these materials and some real applications such as the analysis of minerals, rocks and pharmaceutical products.
3. Kinetics and thermodynamics of adsorption/exchange processes taking place in the materials. These studies help to understand the mechanism of the adsorption/exchange phenomena and predict the possible separations.

The work was carried out mainly at the following places at different stages:

1. Department of Chemistry, Aligarh Muslim University, Aligarh, India.
2. Department of Applied Chemistry, Aligarh Muslim University, Aligarh, India.
3. Bhabha Atomic Research Centre, Trombay, Bombay, India.
4. Department of Chemistry, Roorkee University, Roorkee, India.
5. University of Rome, Rome, Italy.

CURRICULUM VITAE

KRISHNA GOPAL VARSHNEY

READER
APPLIED CHEMISTRY DEPARTMENT
FACULTY OF ENGINEERING & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH - 202 002 (U.P.) INDIA.

Home Address :

Shanti Sadan
18/158, Pakki Sarai
ALIGARH - 202 001, INDIA

DATE OF BIRTH : April 12, 1942

MARITAL STATUS : Married (Three Children)

ACADEMIC QUALIFICATIONS :

Degree	University	Year	Subjects
B.Sc.	Aligarh Muslim University,Aligarh.	1961	Phy.,Chem.,Maths.
M.Sc.	Aligarh Muslim University,Aligarh	1963	Chemistry (Analytical)
Ph.D.	Aligarh Muslim University,Aligarh	1968	Chemistry (Analytical)

PROFESSIONAL EXPERIENCE : (Employment History and Teaching Experience)

Designation	Place	Duration
Associate Lecturer	Z.H. College of Engg. & Tech. AM.U., Aligarh	Aug. - Sept. 1963
Lecturer	Women's College A.M.U.,Aligarh	Jan. - May, 1966
Lecturer	Chemistry Department, A.M.U.,Aligarh	Dec.,1966 - July, 1967
Pool Officer	---do---	April,1970 - Aug.,1971
Lecturer	Z.H.College of Engg.& Tech. A.M.U.,Aligarh	Aug.,1971 - Dec.,1982
Reader	---do---	Jan.,1983 - Continued

COURSE TAUGHT AND CLASSES TAKEN :

(a)	Physical Chemistry (Thermodynamics) -	B.Sc.	- 1966-67
(b)	Analytical Chemistry (Instrumental and Non Instrumental methods of Analysis) -	M.Sc. (As a Lecturer, SRF and Pool Officer)	- 1966-71
(c)	Chemical Instrumentation (Electrochemical Methods of Analysis) -	M.Sc. (Engg.)	- 1973-76
(d)	Materials Science -	M.Sc.(Engg.)	- 1976-83
(e)	Physical/Organic/General Chemistry -	B.Sc.(Engg.) 1st Yr.(5 Yr. Course)	- 1971-84
(f)	Materials Science -	B.Sc.(Engg.) 2nd Yr. (5 Yr Course)	- 1974-83
(g)	Engg.Chemistry -	B.Sc.(Engg.)	- 1983 to date
(h)	Materials Technology -	B.Sc.(Engg.) (IIIrd Yr.(Chemical)	- 1987 to date

Teaching includes Lectures, Tutorials and Practicals.

RESEARCH EXPERIENCE :

(a) Broad Area of Interest - Physico- and Applied Analytical Chemistry.

(b) Fields of Interest - Chromatography/Ion Exchange/ Electrophoresis/ Spectrophotometry.

(c) Field of Current Interest- Inorganic Ion Exchangers with reference to-

(i) Development and Characterization (ii) Chromatographic applications, (iii) Catalytic activity, (iv) Effluent treatment, (v) Control of pollutants, (vi) Metal analysis of pharmaceuticals, (vii) Metal analysis of rocks and alloys, (viii) Adsorption of pesticides, (ix) Thermodynamics and kinetics of adsorption/exchange.

(d) National Associate of UGC for 5 years (1976 - 81)

(e) Research Schemes Completed :

1. Synthesis and Ion-Exchange Behavior of some Phospho- and Arseno-silicates of Tetravalent Metals and their Applications in Water purification and Alloy Analysis

   - CSIR 1981 - 84

2. Synthesis of some Amorphous and Crystalline Inorganic Ion-Exchangers and their Novel Applications.

   - CSIR 1985 - 88

(f) Research Schemes at Hand :

1. Physicochemical Studies of Inorganic Ion-Exchangers and their Applications in the Analysis of Rocks, Minerals and Pharmaceutical Products.

   - U.P. Council of Science & Technology (Lucknow)
   - Since May, 1987

2. Synthesis, Surface Characterization and Catalytic Activity of Inorganic Ion-Exchangers.

   - University Grants Commission (New Delhi)
   - Since 01.02.1988

3. Synthesis and Characterization of some Silica based Inorganic Ion-Exchangers useful in the Treatment of Industrial Effluents and Control of Pollutants.

   - Council of Scientific and Industrial Research (New Delhi)
   - Since 01.06.1988

PUBLICATIONS : :

1. Published 100 research papers in various journals of National and International repute (List attached).

2. Co-editor of a CRC (U.S.A.)Uniscience Publication "Inorganic Ion-Exchangers in Chemical Analysis" (In Press).

3. Co-author in a Chapter "Thin Layer Chromatography of Inorganics and Organometallics" of the "Handbook of Thin Layer Chromatography", Ed. Joseph Sherma and Bernard Fried, Marcel Dekker, U.S.A. (In Press).

4. Member of the Advisory Board of the Handbook of Chromatography (Inorganics),CRC Press (U.S.A.). Chief Editiors: Gunter Zweig and Joseph Sherma; Section Editor: Mohsin Qureshi.

NUMBER OF STUDENTS AWARDED Ph.D. DEGREE :	12	List attached
NUMBER OF STUDENTS AWARDED M.Phil. DEGREE :	15	

NUMBER OF STUDENTS WHO HAVE SUBMITTED Ph.D. THESIS : 1

NUMBER OF STUDENTS WORKING FOR DOCTORAL DEGREE : 5

NUMBER OF POST DOCTORAL STUDENTS AT PRESENT : 1

MEMBERSHIP OF THE LEARNED SOCIETIES

Life Fellow :
1. Indian Sicence Congress Association
2. Indian Chemical Society
3. Indian Council of Chemists
4. Indian Society of Analytical Scientists
5. Indian Association of Nuclear and Allied Chemists.

Member, Executive Committee :
1. Indian Council of Chemists.
2. Indian Society of Analytical Scientists.

ACADEMIC RECOGNITION : Received NOCIL Award for significant contribution on the paper.

"Adsorption Thermodynamics of Carbofuran on Soils and Antimony (V) Silicate Ion Exchanger" presneted in the International Conference on "Pesticides, Toxicity and Risk Assessment", held at the Industrial Toxicology Research Centre, Lucknow, Oct. 27-31, 1985.

CONFERENCES : List attached.

SHORT TERM COURSES ATTENDED : List attached.

VISIT ABROAD : Worked in the University of Rome (Italy) in 1983-84 as a Visiting Professor. The work resulted into the Publication of a research paper entitled "Crystalline Zirconium (IV) Hydrogenerasenate Hydrogenphosphate Monohydrate : Synthesis, Ion Exchange Properties and Thermal Behavior". J.Cehm. Soc. (Dalton's Transaction), 1737, 1985.

FOREIGN ASSIGNMENT : Appointed as a Reader in the University of Maiduguri (Nigeria).

RESEARCH PUBLICATIONS OF Dr. K.G.VARSHNEY

A. During Ph.D. Work

1. Allyl Alcohol as a Sensitive and Specific Reagent for the Detection of Mercurous Ions.
   Analyt.Chem., 36, 2040, 1964.
2. Fast Quantitative Separation of Fe(II) from Fe(III) by Paper Chromatography.
   Analyt.Chem., 38, 1415, 1966.
3. Selective Determination of Iron by Potassium Cyanido-Potassium Ferrocyanide Reagent.
   Analyt.Chem., 39, 1034, 1967.
4. Preparation and Properties of Stannic Tungstate.
   J.Inorg.Nucl.Chem., 30, 3081, 1968.

B. During Post Doctoral Work (As a Junior Author)

1. Quantitative Separation of Magnesium and Palladium from Numerous Metal Ions on Titanium Tungstate Papers by Electrochromatography.
   Sepn.Scie., 6, 559, 1971.
2. Synthesis, Ion Exchange Behaviour and Composition of Tin(IV) Hexacyanoferrate(II).
   J.Chromatogr., 59, 141, 1972.
3. Mercurous Nitrate as a Selective Reagent for the Detection of some Unsaturated Organic Compounds.
   Chim.Analyt., 54, 79, 1972.
4. Synthesis, Ion Exchange Behaviour and Analytical Applications of Stannous Ferrocyanide: Separation of Mg-Ca, Mn-Ni and Y-Th.
   J.Chromatogr., 65, 547, 1972.
5. Synthesis and Ion Exchange Properties of Thermally Stable Titanium(IV) Vanadate: Separation of Sr(II) from Ca(II), Ba(II) and Mg(II).
   Canad.J.Chem., 50, 2071, 1972.

6. Chromatographic Separation of Metal Ions on Stannous-Ferrocyanide Papers.
   Sepn.Scie., 8, 279, 1973.
7. Cation Exchange Studies of Ti(IV), V(V), Fe(III), Nb(V) and UO_2(II) in Formic, Oxalic, Tartaric and Citric acid Media.
   Analyt.Chem., 45, 1283, 1973.
8. Chromatography of 49 Metal Ions on Stannic Antimonate Papers in Dimethyl Sulphoxide-Nitric Acid Systems and Aqueous Nitric Acid Systems.
   Analyt.Chem., 47, 1520, 1975.
9. Thin Layer Chromatography of Metal Ions on Stannic Antimonate in Aqueous and Mixed Solvent Systems containing Dimethyl-sulphoxide: Quantitative Separation of Uranium from Numerous Metal Ions.
   Sepn.Scie., 11, 533, 1976.
10. Electrochromatographic Behaviour of 49 Metal Ions on Stannic Antimonate Papers.
    Ann.Di Chim., 66, 337, 1976.
11. A Solid State Study of the Detection Procedures for Sugars.
    Ann.Di Chim., 66, 495, 1976.
12. Electrochromatographic Behaviour and Separation of Metal Ions on Tin(IV) Tungstate Papers.
    Ann.Di Chim., 66, 557, 1976.
13. Cation Chromatography on Stannic Tungstate Papers: Quantitative Separation of Vanadium from Iron, Titanium, Zirconium and Thorium.
    Chromatographia, 10, 29, 1977.
14. Thin Layer Chromatography of Metal Ions on Stannic Arsenate: Quantitative Separation of Hg(II) from Cd(II), Zn(II) and Cu(II).
    Sepn.Scie., 12, 321, 1977.
15. Cation Chromatography on Stannic Tungstate Thin Layers in DMSO-Acid and Aqueous DMSO Systems: Quantitative Separation of Gold from Numerous Metal Ions.
    Sepn.Scie., 12, 649, 1977.

16. A Novel Quantitative Separation of Cr(III) from Numerous Metal Ions on β-Stannic Arsenate Thin Layers in DMSO-HCl Systems.
Sepn.Scie. & Tech., 13, 321, 1978.

17. Unusual Selectivities of Stannic Arsenate Layers in DMSO-HCl Systems: Separation of Zirconium from Numerous Metal Ions.
Sepn.Scie. & Tech., 13, 917, 1978.

18. Synthesis and Ion-Exchange Behaviour of Nickel and Cobalt Antimonates: Quantitative Separation of Bi(III) from 48 Metal Ions.
J.Chromatogr., 169, 365, 1979.

19. Crystalline Zirconium(IV) Hydrogenarsenate Hydrogenphosphate Monohydrate: Synthesis, Ion Exchange Properties and Thermal Behaviour.
J.Chem.Soc.(Dalton's Transaction), 1737, 1985.

20. Trends in Analytical Chemistry In India.
TrAc, 7, 193, 1988.

C. As a Research Guide (Senior Author)

1. Cation Chromatography on Tin(IV) Hexacyanoferrate(II) Papers in HCl + NH_4Cl Systems: Prediction of Ksp values from Ri values.
Chromatographia, 10, 542, 1977.

2. Amine Sn(II) Hexacyanoferrate(II) as an Inorganic Ion Exchanger.
J.Inorg.Nucl.Chem., 39, 2075, 1977.

3. Anion Exchange Properties of Insoluble Solids: Separation of Chloride from other Halides on AgCl Columns and of Sulphate from Sulphide on Lead Sulphate Columns.
Chromatographia, 10, 682, 1977.

4. Distribution Studies of Metal Ions on Stannic Arsenate in Butanol-HNO_3 Systems: Quantitative Separation of Ni-Fe, Ni-Cu, Cd-Hg and Pb-Hg.
Chromatographia, 11, 660, 1978.

5. Stability and Distribution Studies of Sn(IV) and Cr(III) Arsenophosphates.
   Talanta, 25, 528, 1978.
6. Synthesis and Ion Exchange Properties of Sn(IV) and Cr(III) Arsenophosphates.
   J.Inorg.Nucl.Chem., 41, 241, 1979.
7. Distribution Studies of Metal Ions on Arsenophosphates of Sn(IV) and Cr(III) and on Amine Sn(II) Hexacyanoferrate(II) and Hg(II)-Zn(II).
   Chromatographia, 12, 413, 1979.
8. Silica Based Double Salts as Cation Exchangers-I. Synthesis and Analytical Applications of Ce(IV) Phospho-Silicate.
   J.Liq.Chromatogr., 4, 1245, 1981.
9. Silica Based Double Salts as Cation Exchangers-II. Synthesis and Analytical Applications of Sn(IV) Phospho-Silicate.
   J.Liq.Chromatogr., 4, 915, 1981.
10. Cation Chromatography on Sn(IV) Hexacyanoferrate(II) Papers in Carboxalic Acid, DMSO and HNO_3 Systems: Separation of Metal Ions.
    J.Ind.Chem.Soc., 58, 241, 1981.
11. The Kinetics of Ag^{+}, Cu^{2+}, Sr^{2+}, Ba^{2+} and Y^{3+} Exchange in Arsenophosphate.
    Ind.J.Chem., 20, 841, 1981.
12. Synthesis, Composition and Ion Exchange Behaviour of Zr(IV) and Ti(IV) Arsenophosphates: Separation of Metal Ions.
    Sepn.Scie. & Tech., 16, 793, 1981.
13. pH-Titration and Distribution Studies of Alkali Metals on Amorphous Sn(IV) and Cr(III) Arsenophosphates: Separation of Metal Ions.
    Ann.Di.Chim., 579, 1981.
14. Synthesis, Ion-Exchange Behaviour and Composition of Silica Based Sn(IV) Hexacyanoferrate(II).
    Ind.J.Tech., 19, 457, 1981.
15. Electrochromatographic Studies of Metal Ions on Sn(IV) Hexacyanoferrate(II) Papers: Separation of Metal Ions.
    J.Ind.Chem.Soc., 58, 1025, 1981.

16. Synthesis and Ion-Exchange Properties of Amine Tin(IV) Hexacyanoferrate(II) and its Use in the Separation of Cadmium(II) from Zinc(II), Manganese(II), Magnesium(II) and Aluminium(III).
    Ind.J.Chem., 21A, 398, 1982.
17. Cation-Exchange Study on a Crystalline and Thermally Stable Phase of Antimony Silicate: Effect of Irradiation on its Ion-Exchange Behaviour and Separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II) and Sr(II).
    Sepn.Scie. & Tech., 17(13), 1527, 1982-83.
18. Role of Fertilizers in the Chemical Control of Hookworm.
    Ind.J.Pharmacol., 15, 70, 1982.
19. Influence of Moisture and Porosity of Soil on the Transformation of Haemonchus Contortus Eggs to Infective Larvae.
    Ind.J.Parasit., 7(1), 65, 1983.
20. Galvanotactic Behaviour of Infective Larvae of Haemonchus Contortus.
    Indian J.Parasit., 7(2), 133, 1983.
21. Synthesis, Ion-exchange Behaviour and Analytical Applications of a New, Crystalline and Stable Zirconium(IV) Arsenosilicate Cation Exchanger: Analysis of Some Silicate Rocks.
    Sepn.Scie. & Tech., 18(1), 59, 1983.
22. Adsorption Studies of Alkali Metals on Various Inorganic Ion-Exchange Materials using Radiotracers.
    Radiochem.Radioanalyt.Lett., 58(3), 141, 1983.
23. Quantitative Determination of Iron and Aluminium in some Alloys and Silicate Rocks after a Cation Exchange Separation on Zirconium(IV) Phospho- and Silico-Arsenates.
    J.Liq.Chromatogr., 6(8), 1535, 1983.
24. Analytical Applications of Zr(IV) and Ti(IV) Arsenophosphates as ion-exchangers.
    Talanta, 30(12), 955, 1983.
25. Kinetics of Exchange of Alkaline Earth Metals on Antimony(V) Silicate Cation Exchangers.
    Ind.J.Chem., 22A, 657, 1983.

26. The Separation of Aluminium and Magnesium in Some Antacid Drugs using Zirconium(IV) Phospho- and Silico-Arsenate Columns.
    Analyt.Lett., 16(B9), 685, 1983.
27. Ion-Exchange and Selectivity Behaviour of Thermally Treated and γ-irradiated Phases of Zirconium(IV) Arsenophosphate Cation Exchanger: Separation of Al(III) from some Metal Ions and Removal of Cations from Water.
    Sepn.Scie. & Tech., 18(10), 905, 1983.
28. A Sensitive and Specific Resin-Bead Test for Histidine and its Spectrophotometric Determination using KBr-$KBrO_3$ Reagent.
    Analyt.Lett., 16, 1093, 1983.
29. A Complexo-ion-exchange Method for the Specific Detection of Iron on Zirconium(IV) Arsenophosphate Beads.
    Analyt.Lett., 16(A17), 1381, 1983.
30. Radiation Stability of some Thermally Stable Inorganic Ion Exchangers.
    J.Radioanal.Nucl.Chem., 82(2), 299, 1984.
31. Ion-Exchange Kinetics of Some Metal Pollutants and their Separation on Zirconium(IV) Phospho- and Silico-Arsenate Cation Exchangers.
    Coll.Surf., 9, 189, 1984.
32. Synthesis of a new Thermally Stable Sn(IV) Arsenosilicate Cation Exchanger and its Application for the Column Chromatographic Separation of Metal Ions.
    Ind.J.Tech., 22, 99, 1984.
33. Thermodynamics of Ca^{2+}-H^+ and Mg^{2+}-H^+ Exchanges on Antimony(V) Silicate Cation Exchanger.
    Acta Chim.Hung., 115(4), 403, 1984.
34. Ion-Exchange Kinetics of Alkaline Earths on Zr(IV) Arseno-Silicate Cation Exchanger: Activation Energy as a Linear Function of the Ionic Mobilities and Radii.
    Acta Chim.Hung., 116(1), 69, 1984.
35. Kinetics of Exchange of Transition Metals on Zirconium(IV) and Thorium(IV) Phosphosilicate Cation Exchangers.
    Acta Chim.Hung., 116(1), 103, 1984.

36. A Fast Cation Exchange Separation of Iron(II) and Iron(III) on Zirconium(IV) Arsenophosphate Columns using Potassium Thiocyanate as a Complexing Agent.
J.Liq.Chromatogr., 7, 201, 1984.

37. Kinetics of Exchange of Some Divalent Metal Ions on Phosphosilicates of Zirconium(IV) and Thorium(IV), and Arsenosilicate of Tin(IV).
Indian J.Chem., 25A, 152, 1984.

38. Thermodynamics of Ba^{2+}-H^{+} and Sr^{2+}-H^{+} Exchanges on Antimony(V) Silicate Cation Exchanger.
Proc.Ind.Nat.Scie.Acad., 50A, 75, 1984.

39. Synthesis and Analytical Applications of Thorium(IV) Phospho-Silicate, a new Mercury Selective Cation Exchanger: Effect of Irradiation on its Ion-Exchange Behaviour.
J.Ind.Chem.Soc., 61(3), 220, 1984.

40. A Kinetic Approach to Evaluate the Energy and Entropy of Activation for the Exchange of Alkaline Earth Metal Ions on Tin(IV) Tungstate Cation Exchanger.
Solv.Extr.Ion Exch., 2(6), 923, 1984.

41. Effect of Culture Filtrates of Fungi on the Transformation of Haemonchus Contortus Eggs to Infactive Larvae in Soil.
Ind.J.Parasit., 8(1), 117, 1984.

42. Observation on Transverse Migration of Infective Larvae of Haemonchus in the presence of Neurohumors.
Ind.J.Pharmacol., 16, 38, 1984.

43. Quantitative Separation of Iron from some Multivitamin-Multimineral Formulations using Zirconium(IV) Arsenophosphate Columns.
Analyt.Lett., 17(B18), 2111, 1984.

44. Kinetics of Ion-exchange of Transition Metals on Tin(IV) Arsenosilicate Cation Exchanger.
React.Kinet.Cat.Lett., 28, 27, 1985.

45. Ion-exchange Kinetics of Some Divalent Metal Ions on Crystalline Antimonic Acid and Antimony(V) Silicate Cation Exchangers.
React.Polym., 3, 321, 1985.

46. Ion-Exchange Kinetics of Alkaline Earths on Zirconium(IV) Arsenophosphate: Linear Variation of Energy and Entropy of Activation with the Ionic Radii and Mobilities.
Coll.Surf., 13, 341, 1985.

47. Use of Zirconium(IV) Arsenophosphate Columns for Cation Exchange Separation of Metal Ions Interfering in the Spectrophotometric Determination of Uranium with sodium Diethyl Dithiocarbamate.
J.Liq.Chromatogr., 8(3), 575, 1985.

48. Analytical Application of Zirconium(IV) Arsenophosphate in Metal Analysis of Antacids.
Ind.J.Technol., 23, 114, 1985.

49. Thermodynamics of the Ba(II)-H and Sr(II)-H Exchanges on Zirconium(IV) Phosphosilicate Cation Exchanger.
Proc.Ind.Nat.Scie.Acad., 51, 726, 1985.

50. Chromatography of Alkaline Earths and Transition Metals on Tin(IV) Arsenosilicate and Arsenophosphate Thin Layers in Buffered EDTA solutions.
J.Liq.Chromatogr., 8, 1347, 1985.

51. Adsorption Thermodynamics of Carbofuran on Sandy Clay Loam and Silt Loam Soils.
Ecotox. and Environ. Safety, 10, 309, 1985.

52. A Complexo-Ion Exchange Method for the Sensitive and Selective Detections of Iron(III) and Molybdenum(VI) on Antimony(V) Silicate Beads.
Analyt.Lett., 18(A16), 2033, 1985.

53. Thermodynamics of Ca(II)-H(I) and Mg(II)-H(I) Exchanges on zirconium(IV) Phosphosilicate Cation Exchanger.
Coll.Surf., 16, 207, 1985.

54. Adsorption Thermodynamics of Carbofuran on Antimony(V) Silicate Cation Exchanger.
Ecotoxicology and Environmental Safety, 11, 179, 1986.

55. Evaluation of the Dimensionless Time Parameter for the Diffusion Controlled Exchange of H(I) with some Bivalent Ions.
Coll.Surf., 18, 67, 1986.

56. Influence of Neurohumors on the Mobility and Transverse Migration of Infective Larvae of Haemonchus Contortus.
Ind.J.Pharmacol., 18(2), 95, 1986.

57. Thin Layer Chromatography of Amino Acids on Tin(IV) Arsenosilicate Cation Exchanger in some Buffer Solutions.
Analyt.Lett., 19(A6), 543, 1986.

58. Forward and Reverse Ion Exchange Kinetics for Na^+-H^+ and K^+-H^+ Exchanges on Crystalline Antimony(V) Silicate.
Coll.Surf., 25, 131, 1987.

59. Chromatography of some Transition and Alkaline Earth Metals on Sn(IV) Arsenosilicate and Sn(IV) Arsenophosphate Papers in EDTA Solutions of Varying pH.
Proc.Nat.Acad.Scie., 57, 523, 1987.

60. Synthetic, Kinetic and Analytical Studies on Titanium(IV) Arsenosilicate Ion Exchanger: Separation of Lead from its Synthetic Alloys.
Coll.Surf., 29, 175, 1988.

61. Antimony(V) Arsenophosphate as a Thermally Stable Cation Exchanger: Selective Adsorption of Alkaline Earth and Transition Metal Ions on its Column.
Bull.Chem.Soc., 61, 3693, 1988.

62. Chromatography of Amino Acids on Papers impregnated with Tin(IV) and Thorium(IV) Phosphosilicates: Separation of Basic Amino Acids from others.
Proc.Nat.Acad.Sci., 59(A), II, 364, 1989.

63. Synthesis, Characterization and Ion Exchange Behaviour of Antimony(V) Phosphate: Selective Adsorption of Cadmium and Mercury on its Column.
Ecotox. and Environ.Safety, 18, 1, 1989.

64. Evaluation of the Energy and Entropy of Activation for the Forward and Reverse Exchanges of Alkaline Earth Metals on Antimony(V) Arsenophosphate Cation Exchanger - A Kinetic Approach.
React.Kinet.Catal.Lett., 40, 319, 1989.

65. Forward and Reverse Ion Exchange Equilibria on Antimony(V) Phosphate-I. Evaluation of Various Thermodynamic Parameters for the Exchange of Alkali and Alkaline Earth Metal Ions on its Surface.
Asian J.Chem., 2, 57, 1990.

66. Adsorption Behavior of Antimony(V) Phosphate for α-Amino Acids: Some Binary Separations on its Columns.
Ind.J.Environ.Protection, 9, 574, 1990.

67. Synthesis, Ion Exchange Behaviour and Characterization of Chromium(III) Arsenosilicate Cation Exchanger:
Coll.Surf.

68. Cation Exchange Separation of Iron from Some Liquid Appetite Stimulants and Iron Preparation on Zirconium(IV) Arsenophosphate Columns.
J.Ind.Counc.Chemists,

69. Thermodynamics of the Forward and Reverse Exchanges of Alkaline Earth Metal Ions with H(I) on Antimony(V) Arsenophosphate Cation Exchanger.
Proc.Ind.Nat.Scie.Acad.

70. Evaluation of the Dimensionless Time Parameter for Some Particle Diffusion Controlled Forward and Reverse OH(I)-Anion(I) and OH(I)-Anion(II) Exchanges.
Coll.Surf.

71. Tin(IV) Pyro Antimonate as a Lead Selective Cation Exchanger: Synthesis, Characterization and Analytical Applications.
Bull.Chem.Soc.

72. Adsorption of Tertiary Nitrogen Containing Compounds on Activated Carbon-I: Equilibrium studies of Nicotinic Acid in Aqueous Systems.
Coll.Surf.

73. Adsorption of Tertiary Nitrogen Containing Compounds on Activated Carbon-II: Equilibrium Studies of 2,6-Lutidine in Aqueous Systems.
Coll.Surf.

D. As an Independent Author

1. Some Silica Based Double Salts as Ion Exchangers Useful in the Treatment of Industrial Effluents and Control of Pollutants.

   Ecotox.Environ.Safety, 17, 167, 1989.

2. Inorganic Ion Exchangers as Catalysts.

   Bull.Ind.Soc.Anal.Scientists (In Press).

C H A P T E R - 1

DEVELOPMENT AND SCOPE OF SYNTHETIC INORGANIC ION EXCHANGERS

1.1 INTRODUCTION

Inorganic ion exchangers are receiving increasing attention[1-3] owing to the fact that they are resistant to heat and radiation and can be used for the high temperature separation of ionic components in radioactive wastes, as solid electrolytes and as catalysts. They can be prepared both in the amorphous and crystalline forms. Earlier studies started with the amorphous materials. However, with the synthesis of a crystalline form of zirconium phosphate in 1964 by Clearfield and Stynes by refluxing amorphous product in phosphoric acid for a long time, a spurt of activities took place in the field of crystalline materials. Crystalline materials, besides having a more definite composition, compare favourably with the corresponding amorphous ones as regards thermal degradation and stability towards hydrolysis. Moreover, several crystalline exchangers can exhibit good ion sieve properties and therefore they can be employed to carry out very good separations of inorganic ions of different crystalline radii. However, ion exchange studies with crystalline materials are often complicated by the formation of new crystalline phases and by hysteresis phenomenon. Therefore, amorphous exchangers can be preferred for some particular uses.

As the literature shows, a large number of the inorganic ion exchangers prepared are amorphous in nature. The reason, perhaps, is the easy methods of preparation of such materials and their granular nature suitable for column operations. They can be prepared[2] in the form of granules simply by combining two or more salts forming gelatenous precipitates at room temperature or at a slightly higher temperature with or without refluxing. These granules can be obtained in a range of mesh sizes. The number of possible combinations is very large and most of them have been prepared and their ion exchange properties studied[4]. As a result, these materials have acquired a prominent position in the field of separation science at present. As a

group, they are known to have a great selectivity towards the heavier alkali and alkaline earth metal ions, particularly, cesium. They have an analytical potential for the recovery and concentration of strongly adsorbed trace constituents, which has made their study more interesting. The main efforts have been on the synthesis and characterization of physically and chemically stable ion exchangers, reproducible in behaviour and selective for certain metal ions.

The insoluble acid salts of multivalent metals possessing ion exchange properties can be produced, in general, as gelatinous precipitates by mixing rapidly the elements of groups III, IV, V and VI of the periodic table, usually at room temperature. Sometimes, refluxing is recommended to improve their reproducibility and ion exchange characteristics. The pH is adjusted at 0-1 with the help of either an acid or a base. The precipitate settles slowly to form a gelatinous cake which shrinks on drying and cracks to give a granular product. When immersed in water the granules break down along strain lines with the release of air bubbles which have been entrapped in the gel, accompanied with heat. These granules are stable physically in water, and may be obtained in a range of mesh sizes from several millimeters downwards. The method described is a general method of preparation of the amorphous ion exchangers. Only marginal differences exist in the various methods of preparation given in the literature, and they are in terms of the concentration of the mixing solutions, initial pH of the component solutions and temperature of mixing.

Characterization of amorphous ion exchangers is mainly based on their physical and physicochemical properties, and on ion exchange characteristics. These will be discussed individually.

A. Physical and Physicochemical Characterization: It includes the appearance such as the shape, size and colour of the particles produced. Granular shape is preferred over the

powdered one when column operations are of primary importance. Similarly, size of the granules play an important role in achieving separations and in adjusting the flow rate of the column in a chromatographic process. Uniformity in size can be achieved by sieving into different mesh sizes ranging from 25 to 400, in general. The efficiency of a column is very much affected by the particle size because it governs the number of theoretical plates. The colour of a material is helpful in visualizing the presence of various species on its surface, thus giving some important clues regarding the chemical properties of the substance. Hardness, opaqueness, transparence, shiningness etc. are generally observed for a material in order to ascertain its usefulness under certain specific conditions. Physicochemical methods include the x-ray diffraction (in case of the crystalline materials), IR, and TGA/DTA which give a lot of informations.

B. Ion Exchange Characterization: The real utility of an ion exchanger depends largely on its ion exchange characteristics. Ion exchange capacity, concentration and elution behaviour, pH-titration and distribution behaviour are some of the properties which constitute the ion exchange characteristics of a material.

1. Ion Exchange Capacity

Ion exchange capacity, expressed generally as meq equivalents/dry g or equivalents/Kg, is the measure of the number of replaceable H^+ ions per unit mass of the exchanger. This property is determined generally by the nonequilibrium process i.e. using a column. A column is prepared by carefully packing the solid material (small particles) in a glass tube, usually by adding it to a column filled with solvent or by pouring a slurry of it into the column and allowing this to settle. The column can be mechanically vibrated or the solid material tempered with a long plunger during packing. Care must be taken to keep out air bubbles or channeling will result in the column, rendering it less effective. A sintered glass frit or glass wool is placed in the bottom of the column to support the solid. A buret can be used as the column. A

typical column may range from a few millimeters in diameter and a few centimeters in length to a few centimeters in diameter and several dozen centimeters in length. Preparative columns may have dimensions in feet and yards. They are used for the separation and purification of materials, which may range from a few grams or less to several pounds. Analytical columns, on the other hand, deal with much smaller quantities, usually in the milligram and submilligram range.

2. Concentration and Elution Behaviour

Concentration and elution behaviours of an ion exchanger are also determined by the column process. It is observed that the elution of the H^+-ions from a column depends on the concentration of the eluent. Hence, for a fixed amount of the ion exchange material a curve can be drawn between the concentration of the eluent and the H^+-ions eluted out keeping the rate of elution to a minimum. It gives an optimum concentration of the eluent necessary for a maximum elution of H^+-ions. It depends upon the nature of the ionogenic groups present in the exchanger which, in turn, depends upon the pK_a values of the acids used in its preparation. Sodium or potassium salts such as chlorides or nitrates are taken as eluents, and it is observed that nearly 1M is the optimum concentration generally observed for a maximum elution of H^+-ions from a column containing 1 g of the ion exchanger.

Once the optimum concentration is determined of the eluent, it is necessary to ascertain the optimum volume of the eluent for a complete elution of the H^+-ions from a column of the exchanger. It is achieved by collecting the eluent in equal volumes in several test tubes (for example 5 ml increments). If the flow rate is constant, then samples may be collected at equal time intervals. Automatic fraction collectors can be used for this purpose. After the various fractions are collected, they are analyzed for the H^+-ions by simple titration, and the amount or concentration in each tube is plotted as a function of the tube

number or volume of solvent collected. It gives an idea regarding the maximum volume of the eluent required for almost a complete removal of H^+-ions from a specific column, and thus the efficiency of the column.

3. pH-titrations

Acid salts of multivalent metals are acidic in nature and act as cation exchangers. They can be, therefore, titrated against an alkali as usual. It gives the nature (weak or strong) and the number of exchange sites present in the ion exchanger. An alkali hydroxide is used to neutralize the protons and allow the reaction to go to completion, and a decinormal salt solution of the same alkali metal is used as a supporting electrolyte. A graph plotted between the number of milliequivalents of OH^- ions added and the resultant pH of the mixture at equilibrium is termed as the "pH-titration curve" or the "potentiometric titration curve". It gives the functionality of the ion exchanger. Potentiometric titrations are performed by the usual batch process.[5] It is generally observed that the shape of the titration curve depends upon the time of contact of the exchanger beads with the solution containing OH^- ions, until an equilibrium is obtained, which takes sometimes several days if the system is put at room temperature with intermittant shaking. The equilibration time can be reduced, however, if a constant shaking device is used.

4. Distribution Behaviour

Distribution coefficients (Kd) is the measure of a fractional uptake of metal ions competing for H^+-ions from a solution by an ion exchange material. It is defined as follows:

$$Kd = \frac{I-F}{F} \times \frac{V}{W} \text{ ml g}^{-1}$$

where I = The total amount of the metal ions in the solution initially.

F = The amount of the metal ions left in the solution after equilibrium.

V = Volume of the solution.

W = Weight of the exchanger.

The initial concentration of the electrolyte solution is so adjusted that it does not exceed 3% of the total exchange capacity of the exchanger taken.[6] Kd is an important factor for determining the analytical potential of an ion exchanger. This, alongwith the separation factor, α, point to the possibility of a particular separation on a column of the exchanger. The separation factor, α, is the ratio of the Kd values of the two competing ions in a solution.

REFERENCES

1. Amphlett,C.B., "Inorganic Ion Exchangers", Elsevier Amsterdam (1964).
2. Clearfield,A., (Ed.), "Inorganic Ion Exchange Materials", CRC Press, Inc., Boca Raton, Florida (1982).
3. Qureshi,M. and Varshney,K.G. (Eds.), "Inorganic Ion Exchangers in Chemical Analysis", CRC Press, Inc., Boca Raton, Florida (In Press).
4. Walton,H.F., "Ion Exchange Chromatography" Dowden Hutchinson and Ross, Inc. (1976).
5. Topp,N.E. and Pepper,K.W., J.Chem.Soc.(A), 3299, 1949.
6. Hamaguchi,H., Kuroda,R., Aoki,K., Sugisita,R. and Onuma,N., Talanta, 10, 151, 1963.

1.2 INORGANIC ION EXCHANGERS AS CATALYSTS

K.G.Varshney,
Department of Applied Chemistry,
Faculty of Engineering and Technology,
Aligarh Muslim University,
ALIGARH-202002 (INDIA).

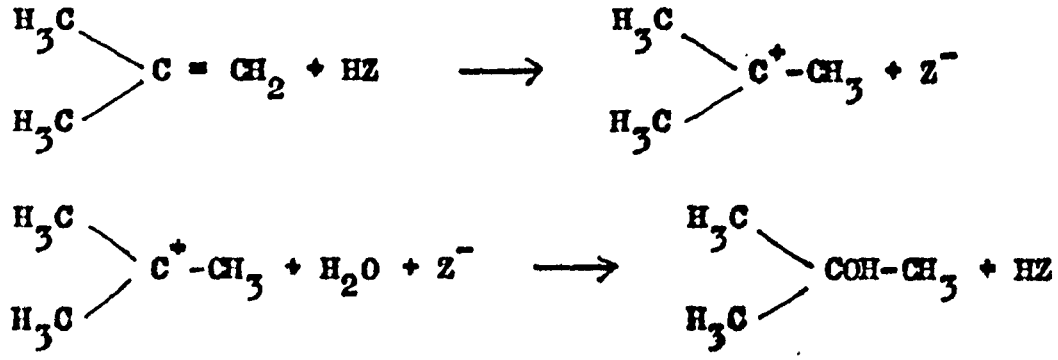
INTRODUCTION

A substance that causes a reaction to proceed more rapidly to equilibrium, and does not itself undergo any change is called a catalyst. It does not change the value of the equilibrium constant. Platinum black, Raney nickel and transition metal complexes such as palladium complexes are widely used as catalysts in many organic reactions. Some new organic and inorganic compounds have also been used as catalysts which are found to be better than platinum and nickel. One such compound is Sr-doped $LaCoO_3$ which operates better than platinum black for the reduction of oxygen and hydrogen in fuel cells at high temperatures (between 150 -300°). Since the reaction occurs on the surface of the metal the surface area plays an important role. Larger the surface area the higher is the catalytic activity. Ion exchangers having a larger surface area and a high dispersion are used as catalysts for many chemical reactions. They are solid insoluble substances which carry some exchangeable ions. These exchangeable ions are known as counter ions and play an important role in catalysis. They are, therefore, catalytically active species. The catalytic activity of ion exchangers thus is directly related to their ion exchange properties. There are two types of catalysed reactions.

(i) Reactions of gases and vapours

These reactions occur at the external or internal surface of porous catalyst where the reactants are activated by being sorbed. In these reactions zeolites and other ion exchangers can be used

as catalysts. For example hydrogenation of isoolefin is catalysed by zeolites:



Here Z^- is a matrix element of the aluminosilicate. This mechanism involves proton transfer from the catalyst which should be acidic to the reactant. Efficient catalysis of gas reactions requires a large surface area of the catalyst. Crystalline inorganic ion exchangers, particularly zeolites are used because their open and rigid pore structure guarantees accessibility of the internal surface and also their great thermal stability as compared to organic resins. According to Helfferich[1] ion exchange resins are of little use in reactions of gases and vapours since the elastic matrix of the resins contracts and closes the pore when the resin is not in contact with the solvent. It should be effective only in solvents owing to the large swelling and thus opening the pores to the reactants.

(ii) Reactions of liquids and solutes

A large number of reactions are subject to the homogeneous catalysis by dissolved electrolytes. In many of these cases the electrolyte is an acid or a base. Dissolved electrolytes are replaced by an ion exchanger which contains catalytically active ions as counter ions. A simple example is the inversion of sucrose catalysed by an ion exchanger in the H^+ form.

Due to the high thermal stability of crystalline inorganic ion exchangers these are introduced as catalysts in many organic reactions such as the dehydration of alcohols. As a rule organic ion exchange resins rather than other ion exchange materials are used for catalysis of liquid phase reactions. The resins are

superior to the inorganic ion exchangers because of the higher mobilities of the reactants and products in the pores of the swollen catalysts. Also the chemical stability of the resins, particularly against acids is usually higher. Serious disadvantages of the organic resins are their limited thermal stability and in reactions involving strong oxidising agents, their insufficient resistance to oxidative decross-linking. For reactions at higher temperatures (above 100°C) and in the presence of oxidising agents such as H_2O_2 the newly developed ion exchangers are likely to be more satisfactory.[2] It is, therefore, worthwhile to deal with the catalytic properties of inorganic ion exchangers.

CLASSIFICATION OF INORGANIC ION EXCHANGERS

According to the Vesely and Pekarek classification[3] inorganic ion exchangers are of the following six types:

1. Hydrous oxides
2. Acid salts of multivalent metals
3. Salts of heteropoly acids
4. Insoluble ferrocyanides
5. Synthetic aluminosilicates
6. Certain other substances, e.g. synthetic apatites, sulphides, alkaline earth sulphates.

Out of the various classes of compounds given above, zirconium phosphate (ZrP) is probably the one whose catalytic properties have received the greatest attention. Therefore, the various aspects of the catalytic behaviour of zirconium phosphate and its analogues especially α-ZrP will be discussed in the following sequence:

1. Description of the crystal structure of ZrP.
2. The properties of ZrP in the H^+ form as a catalyst.
3. The properties of ZrP in the metal exchanged form.
4. The description of the pillard derivatives of ZrP and their catalytic properties.
5. Controvercies in interpretation of the behaviour of inorganic ion exchanger.

The crystalline ZrP has an empirical formula $Zr(HPO_4)_2nH_2O$. It has a layered structure. The different phases of ZrP differ in the inter layer distance and in the number of water molecules present per mole of the substance. Table-1 gives the salient features of the various phases of ZrP.[4]

I. Crystal Structures of α-ZrP[5]

α-ZrP, i.e. $Zr(HPO_4)_2H_2O$, has a layered structure in which the Zr atoms lie nearly in a plane and are bridged by phosphate groups. Three oxygens of each phosphate group are bound to three different Zr atoms, arranged at the apices of a nearby equilateral triangle. The fourth one points away from the layer and bonds to a H^+ atom. Adjacent layers are staggered in a pseudohexagonal fashion so as to form six sided cavities between the layers. The ion exchange behaviour of the less crystalline supports has been interpreted on the basis of these solids having PO_4^{3-} groups shifted or tilted from the equilibrium position in the crystals so as to provide cavities of different sizes.

II. Catalytic Properties of ZrP in H^+-Form

Any systematic determination of the catalytic properties of ZrP must take into account the great variety of forms of this material, P/Zr ratio, crystallinity, phase(s) present under reaction conditions etc., and their influence on the nature of the catalytic sites. Only a few studies have been carried out along these lines as detailed below:

Since ZrPs are solid acids, one of the fundamental properties to be determined in relation to catalytic behaviour is the nature of the acidic surface sites. This was done for α-ZrP by titration with butylamine in isooctane using various indicators with different values of pKa (Benesi Method). It was found that the total number of acid sites (6.2 meq/g) is very close to the exchange capacity of the solid and remains constant irrespective of the crystallinity and heat treatment. The strong acid groups were a small fraction of the total (0.2 to 2 meq) but always much larger than the number of

Table 1: Crystalline ZrP Phases and Their Inter Layer Spacings

Formula	Proposed designation	Inter layer spacing
$Zr(HPO_4)_2H_2O$	α-ZrP	7.56 Å
$Zr(HPO_4)$	β-ZrP	9.40 Å
$Zr(HPO_4)_2H_2O$	γ-ZrP	12.20 Å
$Zr(HPO_4)_2\frac{1}{2}H_2O$	δ-ZrP	7.13 Å
$Zr(HPO_4)_2$	η-ZrP	5.59 Å
$Zr(HPO_4)_2$	z-ZrP	7.41 Å
$Zr(HPO_4)_2$	θ-ZrP	7.37 Å
$Zr(HPO_4)_2.8H_2O$	ξ-ZrP	10.40 Å

P-OH groups on the surface as determined by surface titration. This number increases almost in direct proportion to the surface area and with increase in temperature.

The dehydration of cyclohexanol to cyclohexane using ZrP as catalyst was found to follow the first order kinetics. A plot of the logarithm of the rate constant verus the logarithm of the number of surface protons, in meq/g for catalyst of increasing surface area was linear. Furthermore, when the surface area protons were exchanged out by Cs^+, a drastic reduction in rate was observed. Quinoline poisoning produced similar results. All of this points to Bronsted acid sites as being responsible for catalytic activity. However, the calcined gel, which exhibited almost no Bronsted acidity, was mildly active in the dehydration reaction.[6] Even the Cs^+ and quinoline poisoned samples exhibited some residual activity. Thus, a second type of site, probably of the Lewis acid type, may also be involved.

III. The Catalytic Activity of ZrP in Metal Exchanged Form

1. Synthesis of Methyl Isobutyl Ketone

Methyl isobutyl ketone is an important industrial solvent which is produced in low yields from acetone by a three step process. Recently,[7,8] a one step synthesis was developed which uses a ZrP gel containing about 0.5% Pd. The ZrP apparently dehydrates the acetone to $(CH_3)_2C{=}CHCOCH_3$ which is then hydrogenated by H_2 with the Pd acting as catalyst. A puzzling aspect of this reaction and the vapour phase hydrolysis of chlorobenzene has also been reported which is due to the high dehydration activity of the gel. The catalyst is heated to 450° C before use and at this temperature almost all of the P-OH groups, have split out water to form P-O-P type links. This point bears further study.

2. Catalytic Properties of ZrP in Cu(II) Form

Cations substituted on ZrP catalyse a wide variety of

hydrogenation, hydrolysis, polymerization and oxidation reactions. A copper containing ZrP gel was found[9] to effectively catalyse the vapour phase hydrolysis of chlorobenzene to phenol at 450° C. These studies open a new field of intense current interest, i.e. heterogenization of homogenous catalysts.[5] Efforts have, therefore, been made by Clearfield to study the nature of the Cu(II)-aguo and ammine complexes which form on the surface of the layered inorganic ion exchanger α-ZrP $Zr(HPO_4)_2.H_2O$. He was particularly interested in oxygen carriers in which Co(II) or Cu(II) interacts with molecular oxygen.

Dehydration of surface exchanged Cu(II) followed by adsorption of ammonia leads to the formation of a $Cu(NH_3)_4^{2+}$ complex with a tetragonal symmetry in the inter lamellar region. Following dehydration, the Cu(II) is situated very nearly between two phosphate oxygens that are situated alternatively above and below the planes of Zr atoms. $ZrCu(PO_4)_2$ can also catalyse the oxidative dehydrogenation of cyclohexene.[10] In α-ZrP the protons can be replaced by transition metals which catalyze the variety of reactions. One can also analyze the effect of increased surface area with little change in surface structure. In fact the surface area decreases as a direct function of crystallinity. In the fully crystalline state, the surface is non porous and the surface area can be calculated from the size and shape of the crystallites.

IV. Pillard Organic Derivatives of ZrP and Their Catalytic Properties

Another method of increasing the surface became available through the medium of pillard organic derivatives of ZrP. Alberti et al.[11] prepared compounds of the type $Zr(RPO_3)_2$ and $Zr(ROPO_3)_2$ by simply replacing H_3PO_4 with the acids $RPO_3.H_2$ or $ROPO_3.H_2$ in the synthesis of α-ZrP by the HF-method.[12] This development has opened up new opportunities for the utilization of layered materials as molecular sieves and catalysts. These systems may allow the manipulation of molecular architecture to achieve the desired chemical behaviour.

Subsequently Dines et al.[13] showed that the layers could be pillard or anchored by using diphosphates or diphosphonates. If a mixture of the diphosphate and H_3PO_4 is allowed to react with Zr(IV), monohydrogen phosphate groups are incorporated at many of the sites.

The present interest in the so called pillard zirconium phosphate compounds arises from the fact that the distance between the layers can be varied in an almost continuous manner by changing the length of the R radical. The interlayer region in both α-ZrP and its derivatives is almost completely filled by counter ions, solvated molecules or by R-columns. The available surface area is, therefore, limited to the exterior of the materials and this represents the main drawback in the wide application of these materials. Alberti has, therefore, tried to replace some of the R-pillars by smaller groups. The size and shape of the cavities can be varied by changing the length of the pillars and the ratio between the number of pillars and P-H groups.

V. Controversies in the Interpretation of the Catalytic Behaviour of Inorganic Ion Exchangers

(1) Clearfield and Pack[14] reported that α-ZrP exchanged with Cu(II) ions was a good catalyst for the oxidation of CO and the oxidative dehydrogenation of cyclohexene. They tentatively concluded from ESR study that oxidative dehydrogenation proceeds via the oxidation reduction cycle of Cu(II) ions.

Hattori[15] showed that α-ZrP is a good catalyst for the oxidative dehydrogenation of ethylbenzene without ion exchange. Thus the role of Cu ions in the oxidative dehydrogenation of cyclohexene needs further study.

(2) It has been proposed by Hattori et al. that the catalytic activity of α-ZrP is due to the strong acid sites. However they have not been able to correlate and explain in what manner the catalytic activity is influenced by the number of strong acid groups.

(3) α-ZrP with a reported surface area of 335 M^2/gm was found[16-18] to yield 93 to 99% conversions of C_2-C_4 alcohols to olefins. Significant amounts of methylcyclopentanes were obtained in the dehydration of cyclohexanol.[19]

This stands in contrast to the relative inactivity observed for ZrP gel 0.5 : 48 in the study of Clearfield and Thakur.[20]

(4) The puzzling aspect is the high dehydration activity[21,22] of the gel. The catalyst is a ZrP gel containing 0.5% Pd. It is heated to 450°C before use. At this temperature all the P-OH have split out water to form P-O-P type links, even then the gel shows a high dehydration activity.

(5) A Cu(II) containing ZrP gel was found[23] to effectively catalyse the vapour phase hydrolysis of chlorobenzene to phenol at 450°C. The gels prepared at pH 4 showed the highest activity while the activity fell off sharply for gels prepared at higher or lower pH values. The reasons for this behaviour are obscure and require further study.

(6) The anamolously high surface area of $Ti_{0.2}Zr_{0.8}$ can not be explained in dehydration of cyclohexane by crystalline titanium phosphate and mixed titanium zirconium phosphates[24] and needs further study.

REFERENCES

1. Helfferich,F.G., "Ion exchange", McGraw Hill Book Co., Chap. II p. 519 (1962).
2. Austerweil,G.V., Compt rend, 247, 1726 (1958).
3. Vesely,V. and Pekarek,V., Talanta, 19, 219, 1972.
4. Marinsky,J.A. and Marcus,Y., "Ion exchange and Solv.Extr.", Marcel Dekker, New York, Vol. 5, Chap. I (1973).
5. Clearfield,A. and Quayle,L.R., J.Inorg.Chem., 21, 4197, 1982.
6. Clearfield,A. and Thakur,D., J.Catal., 69, 232, 1981.
7. Watanabe,Y., Matsummura,Y., Izumi,Y., and Mizutani,Y., Bull.Chem.Soc.Japan, 47, 2922, 1974.
8. Onoue,Y., Mizutani,Y., Akiyama,S., Izumi,Y., and Watanabe,Y., Chemtech., 36, Jan. (1977).

9. Izumi,Y., Mizutani,Y., and Akiyama,S., Bull.Chem.Soc.Japan, 52, 3065, 1979.
10. Cheng,H.C. and Clearfield,A., J.Catal., 98, 335, 1980.
11. Alberti,G., Costantino,U., Kornyei,J. and Giovagnotti,M.L., React.Polymers, 4, 1, 1985.
12. Alberti,G. and Costantino,U., J.Mol.Cat., 27, 235, 1984.
13. Dines,M.B., Digiacomo,P.M., Callahan,K.P., Griffith,P.C., Lane,R.H. and Cooksey,R.E., ACS Symp.Ser.No. 192, Am.Chem. Soc.Washington,D.C., 1982, Chap. 13.
14. Clearfield,A. and Pack,S.P., J.Catal., 51, 431, 1978.
15. Hattori,T., Hanoi,H. and Murakami,Y., J.Catal., 56, 294, 1979.
16. Balandin,A.A., Vest Mosk.Univ., 4, 871, 1957.
17. Balandin,A.A., Kukina,A.I., Malenberg,N.E. and Ermilova,M.M., Dockl.Akad Nauk SSSR, 161, 851, 1965.
18. Malenberg,N.E., Kukina,A.I. and Fadieva,T.N., Vest Mosk Univ.Ser.II Khim., 21, 107, 1966.
19. Sharf,V.Z., Nekrasov,A.S. and Nemkova,L.V., Friedlin L.Kh., Izvest Akad.Nauk SSSR Ser.Khim., I 46 (1967).
20. Clearfield,A. and Thakur,D.S., J.Catal., 65, 185, 1980.
21. Watanabe,Y., Matsumura,Y., Izumi,Y. and Mizutani,Y., Bull.Chem.Soc.Japan, 47, 2922, 1974.
22. Onoue,Y., Mizutani,Y., Akiyama,S., Izumi,Y. and Watanshe,Y., Chem.Tech., 36, Jan 1977.
23. Izumi,Y. and Mizutani,Y., Bull.Chem.Soc.Japan, 52, 3065, 1979.
24. Clearfield,A. and Frianeza,T.N., J.Catal., 85, 398, 1984.

ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY 16, 000–000 (1988)

1.3

Some Silica-Based Double Salts as Ion Exchangers Useful in the Treatment of Industrial Effluents and Control of Pollutants[1]

K. G. VARSHNEY

Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001, India

Received March 3, 1988

A systematic comparative study has been performed on the various double salts based on silica. They are found to be more stable chemically and thermally than single salts of this type. Furthermore, these materials have a better selectivity for some pollutants chiefly found in the effluents of dyestuff and plating industries. The purpose of preparing a series of such materials in this study has been to evaluate their comparative usefulness under the varying conditions of pollution. The materials have been characterized on the basis of analytical studies such as chemical composition, pH titration, IR, X-ray, and TGA.

INTRODUCTION

Water pollution due to release of industrial waste waters has already become a serious problem. The common practice adopted so far includes the discharge of untreated or partially treated industrial waste waters into public sewers, rivers, the sea, and on land. Heavy metals, when present in water in concentrations higher than the permitted range, are injurious to health. Ion exchange is a well-established analytical tool for the separation of metal ions. Among the earliest exchangers were aluminosilicates such as leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) which can reversibly and stoichiometrically exchange potassium for sodium, calcium, ammonium, or other ions. Other inorganic ion exchangers include the phosphates, molybdates, tungstates, vanadates of tetravalent metals, and salts of heteropoly acids. These materials are generally the cation exchangers. They have shown promise in separation science mainly because they are more stable at elevated temperatures and under strong radiation.

Inorganic ion exchangers based on silicon have an added advantage in that they are, in general, also chemically stable (Varshney *et al.*, 1983; Varshney and Premadas, 1981a,b). The various silica-based inorganic ion exchangers prepared in these laboratories have demonstrated special selectivity for some polluting metals such as Cu(II), Pb(II), VO(II), Zn(II), Mg(II), Hg(II), Cd(II), and As(V). Hence, they can well be utilized for the removal of these metals from industrial effluents. This paper gives a comparative account of such materials and their potential for such a purpose.

EXPERIMENTAL

Reagents and Chemicals

All the reagents and chemicals used in these studies were of Analar grade.

[1] This paper was presented at the 75th session of the Indian Science Congress held at the University of Poona, January 7–12, 1988.

001 0147-6513/88 $3.00

TABLE 1

Na^+ ION EXCHANGE CAPACITY OF THE VARIOUS ION EXCHANGERS PREPARED

Sl. no.	Name of the ion exchanger	Abbreviated name	Ion exchange capacity (meq/g)
1.	Stannic arsenosilicate	SAS	1.20
2.	Stannic phosphosilicate	SPS	1.40
3.	Zirconium Arsenosilicate	ZAS	1.20
4.	Zirconium phosphosilicate	ZPS	2.19
5.	Thorium arsenosilicate	TAS	1.30
6.	Thorium phosphosilicate	TPS	1.66

Instrumentation

pH measurements were made on an Elico Model LI-10 pH meter. IR studies were performed on a Beckman IR-20 spectrophotometer. X-ray studies were made on a Philips X-ray unit and thermogravimetry was done on a modern TGA balance of the F.C.I. Ltd., India.

Synthesis of the Ion Exchange Materials

Samples of the various heteropoly acid salts based on Sn, Zr, Th, As, Si, and P were prepared as follows. Decimolar aqueous solutions of $SiO_2 \cdot x H_2O$ (dissolved in a minimum quantity of NaOH) and an acid (H_3AsO_4 or H_3PO_4) were mixed in a volume ratio 1:1 with constant stirring. One liter of this homogeneous mixture was mixed slowly, with constant stirring, with 1 liter of a decimolar aqueous solution of $SnCl_4 \cdot 5H_2O$, $ZrOCl_2 \cdot 8H_2O$, or $Th(NO_3)_4 \cdot 6H_2O$ and the pH adjusted to ~0 to 1. The precipitate thus obtained was filtered, washed with demineralized water (DMW) to pH 6–7, and dried at ~100°C. It was then immersed in DMW to obtain granules which were converted to the H^+ form by adding 2 *M* HNO_3 for several hours, replacing the supernatant liquid intermittently. After being washed with DMW to remove excess acid, the material was again dried in an oven. It was now ready for column operation. Particles of different mesh sizes were obtained using various sieves.

Ion Exchange Capacity

The total Na^+ ion exchange capacity of the material was determined by the column process using 100–150 mesh sized particles. A 0.2 *M* aqueous solution of NaCl or $NaNO_3$ was passed through the ion exchange bed prepared with 1 g of the ion exchanger in H^+ form in an ordinary macroburette, at a very slow rate (10–12 drops per minute) until the pH of the effluent became 6–7. The effluent, which contained the H^+ ions, was titrated against a standard NaOH solution to determine the total amount of H^+ ions released by the ion exchanger. It gives the total ion exchange capacity in terms of milliequivalents per gram of the material. The results are summarized in Table 1.

TABLE 2

SPECIAL SELECTIVITY OF THE VARIOUS ION EXCHANGE MATERIALS FOR THE METAL IONS

Ion exchanger	Selectivity for the metal ions
SAS	Pb(II), V(O)(II), Cu(II)
ZAS	Cd(II), Pb(II), Zn(II), Ni(II), Co(II), Al(III), Fe(III)
TAS	Hg(II), Pb(II), Ba(II)
SPS	Fe(III), Al(III), Pb(II), As(III)
ZPS	Pb(II), Zn(II), Fe(III), Ca(II), Mg(II), As(III)
TPS	Hg(II), Pb(II), Ba(II), Fe(III), Co(II), As(III)

Composition

Stannic arsenosilicate. Five hundred micrograms of the exchanger was boiled with 20 ml HCl to dissolve the arsenate and tin present in the compound. The undissolved silica was filtered out and determined gravimetrically (Vogel, 1978). H_2S gas was then passed through the filtrate to precipitate tin and arsenic as sulfides which were treated with HCl to dissolve tin. Tin was determined volumetrically (Kolthoff and Belcher, 1938) with $K_2Cr_2O_7$. The undissolved precipitate containing arsenic was dissolved in NaOH and titrated against thiocyanate (Furman, 1963). The molar composition of the compound was 1:1:1 for Sn:As:Si.

Zirconium arsenosilicate. Five hundred milligrams of the exchanger was boiled with 20 ml of HCl as above to dissolve arsenate and zirconium present in the compound. Zirconium was determined gravimetrically (Alberti *et al.*, 1973) while arsenic and silica were determined as above. The molar composition was found to be 1:2:1 for Zr:As:Si.

Thorium phosphosilicate. The material was dissolved as described above and thorium determined as ThO_2 by the standard method (Vogel, 1978). The molar composition was found to be 1:2:1 for Th:P:Si.

The compositions of stannic phosphosilicate, zirconium phosphosilicate, and thorium arsenosilicate were also determined by the above methods. Their respective molar ratios for the three elements were obtained as 1:1:1, 1:2:1, and 1:2:1.

Elution Behavior

The elution behavior of all the samples was determined as usual by the column process. All show similar behavior in that they rapidly release the H^+ ions almost completely (95%) in the first 70 ml of the eluant (0.1 *M* NaCl) from a column of 1 g of exchanger. Beyond 70 ml the exchange process appears to be slowed appreciably as it took another 150 ml of the eluant for the exchange of the rest (5%) of the H^+ ions.

Characterization of the Ion Exchangers

pH titrations. These were performed by Topp and Pepper's method (1949) by placing 500 mg of the exchanger in several 250-ml conical flasks followed by equimolar

solutions of alkali metal chlorides in different volume ratios, the final volume being 50 ml. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of the OH^- added. Invariably for all the materials the pH titration curves show a similar trend; i.e., they show two inflections as expected from the double salts under study.

IR studies. IR spectra indicate the presence of the various functional groups, viz. H_2O (both external and structural) and metal oxygen in the material.

X-ray studies. They indicate that all the materials produced are amorphous in nature.

TGA studies. These studies coupled with the chemical analysis point to the following structural formulae of the compounds,

SAS	$SnO_2 \cdot H_3AsO_4 \cdot SiO_2 \cdot nH_2O$
ZAS	$Zr(HAsO_4)_2 \cdot SiO_2 \cdot nH_2O$
TAS	$Th(HAsO_4)_2 \cdot SiO_2 \cdot nH_2O$
SPS	$SnO_2 \cdot H_3PO_4 \cdot SiO_2 \cdot nH_2O$
ZPS	$Zr(HPO_4)_2 \cdot SiO_2 \cdot nH_2O$
TPS	$Th(HPO_4)_2 \cdot SiO_2 \cdot nH_2O$

where n has a value ranging from 2 to 4.

Distribution Studies

Two hundred and fifty milligrams of the exchanger beads in H^+ form was equilibrated with 25 ml of the selected solvent, either by shaking for 3–4 hr or by keeping it at room temperature for 24 hr. The initial metal concentration in the solution was adjusted so that it did not exceed 3% of the total iec of the material. The determinations were carried out volumetrically using EDTA as the titrant (Reilley *et al.*, 1959). For alkali metals the tracer technique was used by employing the following isotopes (half-life periods in parentheses): ^{24}Na (15 hr), ^{42}K (12.5 hr), ^{86}Rb (18 days), ^{137}Cs (30.2 years).

The K_d values were obtained by

$$K_d = \frac{I - F}{F} \times \frac{V}{A} \text{(ml/g)}.$$

where I is the initial amount of the metal ion in the solution phase, F is the final amount of the metal ion in the solution phase, V is the volume of the solution (ml), and A is the amount of the exchanger (g). On the basis of these studies the materials under study were found to be selective for certain metal ions as shown in Table 2.

CONCLUSIONS

As these studies point out, inorganic ion exchangers have the advantage of being specially selective for certain metal ions. From Table 2 it is clear that the various materials studied show a high selectivity for most of the pollutants. These metal ions are common in the industrial effluents and are hazardous to one's health if present in a concentration higher than the limit permitted. Thus, by selecting a particular ion exchanger we can separate the undesired metal from the effluents. Since inorganic

ion exchangers are stable at high temperatures and under strong radiation, they have the added advantage of also being useful under such conditions.

REFERENCES

ALBERTI, G., COSTANTINO, U., ALLULLI, S., AND MASSUCCI, M. A. (1973). *J. Inorg. Nucl. Chem.* **38**, 1339.

FURMAN, N. H. (1963). *Standard Methods of Chemical Analysis*, 6th ed., Vol. 1, p. 117. Van Nostrand, Princeton.

KOLTHOFF, I. M., AND BELCHER, R. (1938). *Volumetric Analysis*, Vol. 3, p. 196. Interscience, New York.

REILLEY, C. N., SCHMID, R. W., AND FAWZYS. (1959). *J. Chem. Educ.* **36**, 555.

TOPP, N. E., AND PEPPER, K. W. *J. Chem. Soc.*, 3299 (1949)

VARSHNEY, K. G., AGARWAL, S., AND VARSHNEY, K. (1983). *Sep. Sci. Technol.* **18**, 59.

VARSHNEY, K. G., AND PREMADAS, A. (1981a). *J. Liq. Chromatogr.* **4**, 1245.

VARSHNEY, K. G., AND PREMADAS, A. (1981b). *J. Liq. Chromatogr.* **4**, 915.

VOGEL, A. I. (1978). *Text Book of Quantitative Inorganic Analysis*, 4th ed., p. 501. The Chaucer Press Ltd., Hungary.

VOGEL, A. I. (1978). *Text Book of Quantitative Inorganic Analysis*, 4th ed., p. 885. The Chaucer Press Ltd., Hungary.

C H A P T E R - 2

SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATIONS OF SOME INORGANIC ION EXCHANGERS

March, 1990] Bull. Chem. Soc. Jpn., 63, 0000—0000 (1990) GG6—1

2.1 Tin(IV) Antimonate as a Lead-Selective Cation Exchanger: Synthesis, Characterization, and Analytical Applications

K. G. Varshney* and Uptna Gupta
Department of Applied Chemistry, Faculty of Engineering and Technology,
Aligarh Muslim University, Aligarh-202002, India
(Received July 19, 1989)

A new phase of a lead-selective cation exchange material, tin(IV) antimonate has been prepared, which possesses a good column exchange capacity (2.4 mequiv g^{-1}). Its characterization has been done on the basis of its ion-exchange characteristics and some instrumental studies such as TGA, IR, and X-ray diffraction. The utility of the material has been demonstrated by achieving some binary separations of metal ions on its column, such as Al(III)-Pb(II), Mg(II)-Pb(II), Fe(III)-Pb(II), Al(III)-Fe(III), Mg(II)-Al(III), and Mg(II)-Fe(III). Maximum limits of the column's loading capacity have also been evaluated for all metal ions.

Although a large number of inorganic ion exchangers have been prepared and studied so far,[1] there is still need to obtain a material which may have a good ion-exchange capacity, reproducible properties, stability, and selectivity for a particular ion. These properties are important for a better utility of a material in separation science. Tin(IV)-based inorganic ion exchangers[2-10] generally possess a greater stability both chemical and thermal as compared to the other materials of this class. The present study was undertaken to obtain an ion exchanger, superior in ion-exchange properties and stability over other similar materials.

Tin(IV) antimonate has been found to have a satisfactory behavior in this regard. It has been found to have a high selectivity for lead which is a chief polluting metal in the atmosphere. The common source of lead poisoning is the exhaust fumes from cars. About ninety percent of the lead present in the atmosphere comes from petrol fumes. Its accumulation in body leads to the poisoning and produces chronic illness characterized by severe anaemia and changes in the kidneys and arteries.

The following pages summarize the synthesis, characterization and analytical applications of tin(IV) antimonate. Its utility has also been explored for the quantitative separation of lead(II) from some binary mixtures on its column. A tentative structure of the compound has also suggested on the basis of these studies and IR spectroscopy.

Experimental

Reagents. The tin(IV) chloride used in this study was a C. D. H. (A. R.) product, while the potassium antimonate was a Loba Chemie product. All other reagents and chemicals were of Analar grade.

Apparatus. Spectrophotometry, pH metry, X-ray diffraction, and IR studies were performed by using a Bausch and Lomb Spectronic-20, spectrophotometer, an Elico pH-meter, Model LI-10, a Philips X-ray diffraction unit with a Mo $K\alpha$ target, and a Perkin Elmer spectrophotometer, Model-783, respectively. Heating effect on the ion-exchange capacity and weight loss was studied manually in a muffle furnace.

Preparation of the Reagent Solutions. A solution (0.05 M; 1 M=1 mol dm^{-3}) of tin(IV) chloride ($SnCl_4 \cdot 5H_2O$) was prepared directly in deionized water, obtained by passing the tap water through a deionizer plant (CA-20/U and CA-60/U). Potassium antimonate [$KSb(OH)_6$] was dissolved in 5.8 M HCl solution to obtain a 0.05 M solution.

Synthesis of the Ion-Exchange Material. A number of samples of tin(IV) antimonate were prepared by mixing the solutions of tin(IV) chloride (0.05 M) and potassium antimonate (0.05 M) in different volume ratios, such as 1:1, 1:2, 1:3, and 2:1. The pH of the resulting gel was fixed in the range 0—1 by adding aqueous ammonia with constant stirring. The gel thus obtained was kept for 24 hours at room temperature (ca. 30 °C) and filtered by suction. The excess acid was removed by washing with deionized water and the material was dried in an air oven at 45 °C. It was then cracked into small granules by putting in deionized water. The granules so obtained were of the uniform size suitable for column operation. They were converted into the H^+-form by treating with 1 M HNO_3 for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with a fresh acid. The material thus obtained was finally washed to remove the excess acid and then dried at 45 °C. It was then sieved to obtain particles of uniform size (50—72 mesh) before using for further studies. Following four samples were obtained possessing different Na^+ ion-exchange capacity shown in parantheses corresponding to the four mixing volume ratios as indicated above:

TA-1 (1.2), TA-2 (2.4), TA-3 (2.19), TA-4 (0.90)

All these samples were powdery in nature and white in color except the TA-1 which was light yellow. On the basis of its capacity and apparent stability in acids and bases, sample TA-2 was selected for all the studies.

Ion Exchange Capacity (i.e.c.). The i.e.c. was determined as usual by the column process taking 1 g of the exchanger (H^+-form) in a glass tube of internal diameter (i.d.) ca. 1 cm, fitted with the glass wool at its bottom and passing through it the eluant (ca. 250 ml) and maintaining a very slow flow rate (ca. 0.5 ml min^{-1}). The effluent was titrated against a standard alkali solution to find out the total H^+ ions eluted. The values of the i.e.c. in mequiv g^{-1} for various metal ions are given below:

Li^+—2.17, Na^+—2.40, K^+—1.95, Mg^{2+}—2.2, Ca^{2+}—3.12, Sr^{2+}—3.44, Ba^{2+}—3.3, NH_4^+—4.93

Effect of Eluant Concentration on the i.e.c. The extent of elution was found to be dependent on the concentration of the eluant. Hence, a fixed volume (250 ml) of the $NaNO_3$ solution of varying concentrations was passed through a column containing 1 g of the exchanger keeping a standard (0.5 ml min^{-1}) flow rate and effluent was titrated against a standard alkali solution for the H^+ ions eluted out. The optimum concentration of the eluant for a complete elution of H^+ ions in 250 ml was found to be 1 M.

Elution Behavior. Since the optimum concentration for a complete elution was observed to be 1 M, a column containing 1 g exchanger was eluted with a $NaNO_3$ solution of 1 M concentration in different 10 ml fractions with a minimum flow rate as described above. This experiment was conducted to find out the minimum volume necessary for a complete elution of the H^+ ions, which reflects the efficiency of the column. The column required 110 ml of the eluant.

Composition. 100 mg of the powdered sample was dissolved in a minimum amount of concentrated HCl. The solution was then diluted to 250 ml with 4 M HCl and the amount of tin and antimony was determined as follows:

(a) Determination of Tin: Tin was precipitated with a freshly prepared 6% aqueous solution of cupferron from an acidic solution cooled at 10 °C. It was filtered through a lose texture paper containing a small amount of paper pulp. The paper and precipitates were thoroughly washed, first with a cold H_2SO_4 solution (1:9) containing 1 g of cupferron/litre and then with a cold dilute cupferron solution (1 g l^{-1}), ignited and weighed as SnO_2.[11]

(b) Determination of Antimony: The filtrate was analyzed for antimony after destroying cupferron with perchloric acid. It was evaporated to dryness and the residue was collected in a weighed crucible, blasted in a muffle furnace at 900 °C and weighed as Sb_2O_4.

These studies suggest a molar composition of the compound as Sn:Sb=2:11.

Chemical Stability. The solubility of tin(IV) antimonate in various solvents was determined by the method given below:

200 mg portions of the material were kept with 20 ml of the solvent for 24 hours at room temperature with intermittent shaking. Antimony was determined quantitatively in the supernatant liquid as follows:

To the 2 ml portion of the above solution were added 1.0 ml of 9 M H_2SO_4 and 5 ml of KI reagent (11.2 g of KI+2 g of ascorbic acid in 100 ml water). The color so developed was diluted to 10 ml with water in a standard volumetric flask and the absorbance was measured after 2—3 minutes at 425 nm against a reagent blank.[12]

The amount in ppm of antimony found in the various solvents after the above treatment are given below in parentheses:

DMW (1.71), 1 M CH_3COOH (1.11), 2 M HCl (2.05), 4 M HCl (4.09), 1 M HNO_3 (0.77), 2 M HNO_3 (1.02), 4 M HNO_3 (1.37), 1 M H_2SO_4 (1.24), 2 M H_2SO_4 (2.44), 1 M $HClO_4$ (0.68), 2 M $HClO_4$ (0.94), 0.1 M NaOH (0.98), 1 M $NaNO_3$ (0.08), 1 M HNO_3 (0.21), 1 M NH_4NO_3 (0.21).

It dissolved appreciably in 0.1 M KOH solution.

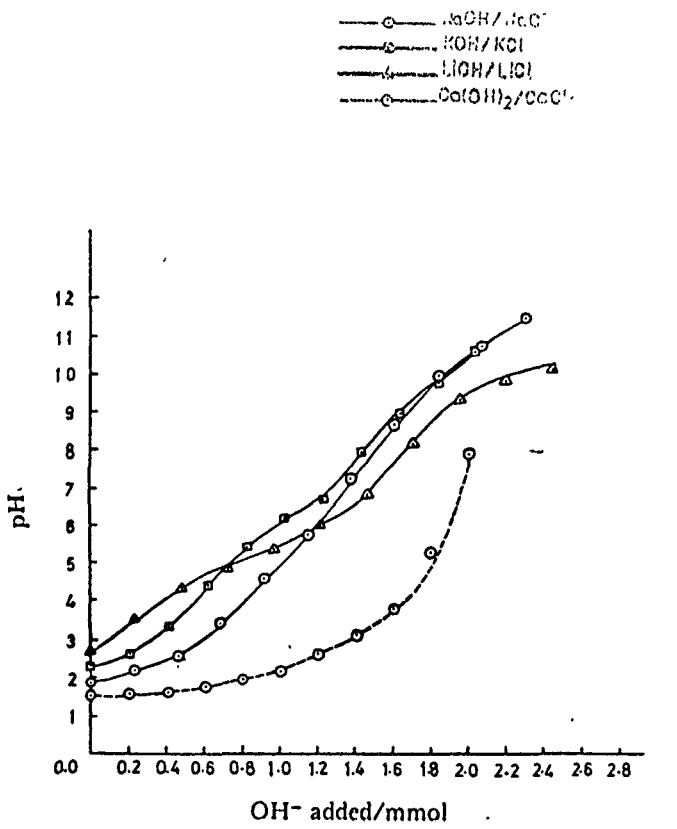


Fig. 1. Equilibrium pH titration curves of tin(IV) antimonate.

pH Titrations. pH titrations were performed by the method of Topp and Pepper[13] 500 mg of the exchanger were placed in each of the several 250 ml conical flasks, followed by the equimolar solutions of alkali and alkaline earth metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml, to maintain the ionic strength constant. The pH of the solutions was recorded after 24 hours to find out the time required for equilibrium. It was observed that the equilibrium was achieved in 12 days. Figure 1 shows the pH-titration curves after keeping the mixtures for such a time period.

Thermal Analysis. For thermal stability several 1 g portions of the exchanger were heated for 1 hour each at various temperatures in a muffle furnace, and the Na^+ ion-exchange capacity in mequiv/dry g was determined as usual by the column process at room temperature. The results are summarized below:

45 °C—2.40; 100 °C—2.40; 200 °C—2.05; 400 °C—1.90; 600 °C—1.00; 800 °C—0.98.

The same sample was also heated at 400 and 800 °C for 4 hours each resulting to the i.e.c. as 1.50 and 0.55 mequiv/dry g respectively. No change in color was observed upto 200 °C. Above this temperature the color changed to light yellow, yellow, and dirty yellow at the temperatures mentioned above in that order.

For studying the weight loss in the material, 50 mg sample was heated as above at various temperatures for an hour each and weight loss recorded. It was repeated to assure the

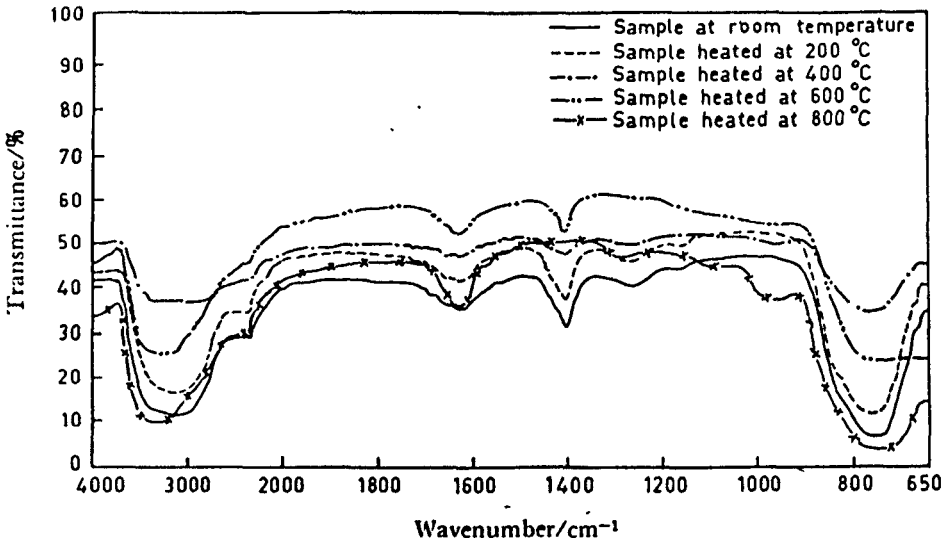


Fig. 2. IR spectra of normal and heated samples of tin(IV) antimonate cation exchanger.

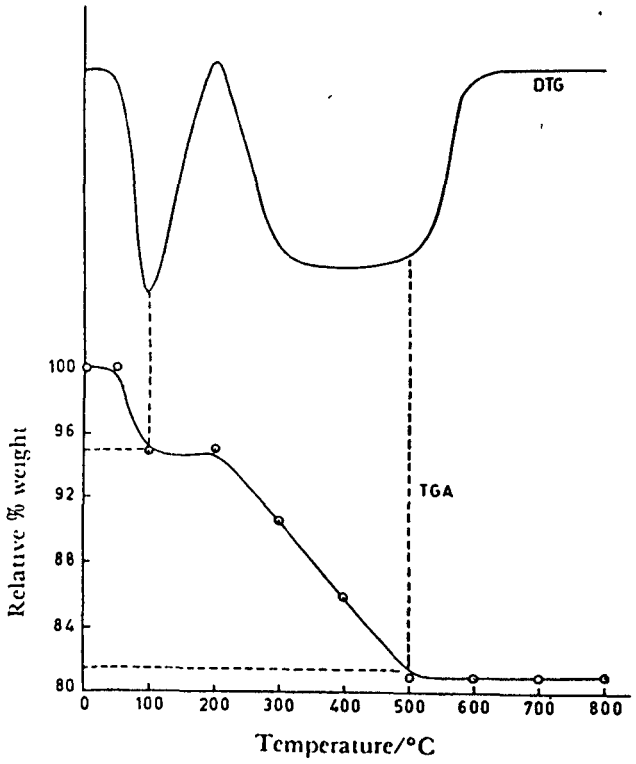


Fig. 3. Thermogravimetric (TGA) and differential thermogravimetric (DTG) curves of tin (IV) antimonate.

reproducibility. Figure 3 shows the thermogram and its differential (DTG).

IR Studies. The IR spectra of tin(IV) antimonate were taken by the KBr disc method and are shown in Fig. 2, for the various samples heated at different temperatures.

Distribution Studies. Distribution studies were performed on a sample of tin(IV) antimonate (TA-2) for different metal ions in various solvents as follows:

200 mg of the exchanger beads in H^+-form were equilibrated with the selected solvents (20 ml) by keeping it at room temperature for 24 hours. The initial metal ion concentration was so adjusted that it may not exceed 3% of the total ion-exchange capacity of the material and the determination was carried out volumetrically using EDTA as titrant,[14] while the concentration of alkali metal ions was determined by the flame photometer.

The K_d values, as summarized in Table 1, were obtained by the formula

$$K_d = \frac{I - F}{F} \times \frac{V}{A} \quad (\text{ml g}^{-1})$$

where

I=Initial amount of the metal ion in the solution phase.
F=Final amount of the metal ion in the solution phase.
V=Volume of the solution (ml).
A=Amount of the exchanger (g).

Separations Achieved. The 60—100 mesh sized particles of the exchanger (2 g) in H^+-form were used for the column separation in a glass tube having an internal diameter of ca. 0.6 cm. The column was washed thoroughly with deionized water and the mixture to be separated was loaded on it, maintaining a flow rate of ca. 2—3 drops/min. The separation was achieved by passing a suitable solvent through the column as eluant and the metal ions in the effluent were determined quantitatively by EDTA titrations. The salient features of these separations are given in Table 2 and Fig. 4.

Discussion

The most exciting feature of these studies is the unusually high ion-exchange capacity of the material, prepared as an inorganic ion exchanger. It appears that the tin(IV) antimonate prepared in these studies is superior to the other tin(IV) based inorganic ion exchangers in terms of their i.e.c. and thermal stability[2-10] as a comparison shows. A study of the

Table 1 K_d Values of Some Common Metal Ions on Tin(IV) Antimonate in Various Media

Metal ion	$K_d \times 10^{-2}$ Solvent								
	Deionized water	0.01 M HNO_3	0.1 M HNO_3	1 M HNO_3	0.01 M $HClO_4$	0.1 M $HClO_4$	1 M $HClO_4$	1 M NH_4NO_3	1 M $NaNO_3$
Na(I)	69.0	13.0	6.8	4.0	13	6.8	4.0	2.5	0.0
K(I)	34.0	6.7	3.3	2.3	7.0	4.0	2.0	1.3	0.97
Mg(II)	7.1	3.1	1.0	1.0	1.7	1.0	0.62	0.62	0.62
Ca(II)	7.4	7.4	7.4	3.1	7.4	7.4	7.4	3.1	3.1
Sr(II)	7.0	7.0	7.0	7.0	7.0	7.0	7.0	3.0	3.0
Ba(II)	5.3	5.3	5.3	2.0	5.3	5.3	2.0	2.0	1.0
Al(III)	4.0	4.0	0.0	0.25	4.0	1.5	4.0	0.67	1.5
Mn(II)	7.0	7.0	3.0	1.7	7.0	3.0	1.0	1.7	1.0
Fe(III)	74.0	74.0	6.5	6.5	6.5	2.8	6.5	6.5	6.5
Co(II)	7.5	7.5	1.8	3.3	7.5	3.3	84.0	3.3	7.5
Ni(II)	80.0	7.1	1.0	1.7	7.1	1.0	80.0	1.0	1.7
Cu(II)	69.0	6.0	6.0	2.3	6.0	6.0	5.5	5.5	5.5
Zn(II)	8.9	8.9	4.0	2.3	8.9	8.9	8.9	4.0	4.0
Cd(II)	80.0	7.1	3.0	3.0	7.1	3.0	7.1	7.1	7.1
Hg(II)	4.0	4.0	1.5	1.5	4.0	0.67	0.67	4.0	1.5
Pb(II)	210.0	210.0	20.0	210.0	210.0	210.0	210.0	20.0	20.0
Bi(III)	—	—	89.0	8.0	—	89.0	89.0	—	—

(—)=Not detectable

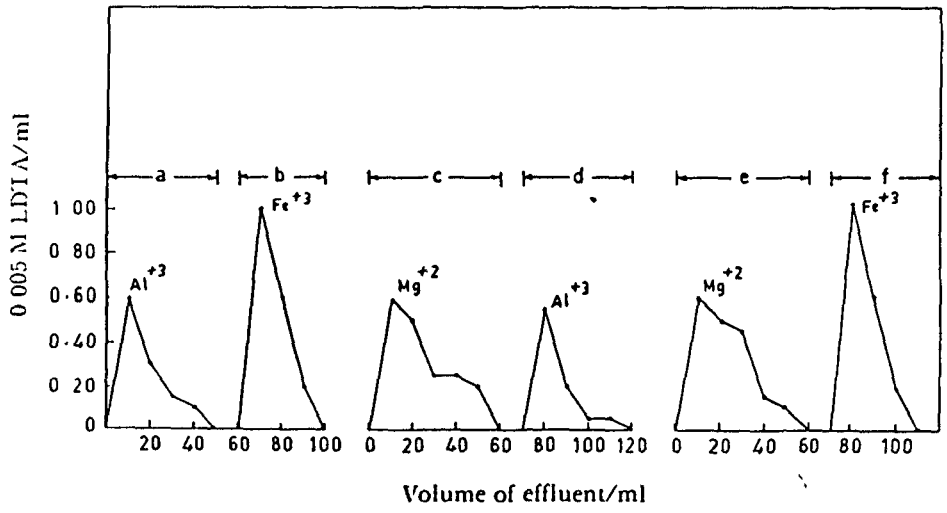


Fig 4 Separation of Al^{3+} from Fe^{3+}, Mg^{2+} from Al^{3+}, and Mg^{2+} from Fe^{3+} on tin(IV) antimonate columns: (a) and (d), 1 M HNO_3, (b) and (f), 2 M HCl+2 M NH_4Cl, (c) and (e), 0.1 M $HClO_4$.

percent retention of the i.e.c. on heating to various temperatures indicates that the material (TA-2) does not lose its i.e.c. upto 100 °C. It retains about 41% of its i.e.c. even on heating upto 800 °C which is a remarkable feature. The mixed oxides produced on heating the material upto such a high temperature might be converted into their hydrated forms, when the material is treated with water, which may be responsible for the ion exchange behavior. Another important feature of this ion exchanger is its reproducible nature. It is observed that tin(IV) antimonate obtained in various batches does not show any appreciable deviation in its ion-exchange properties. Chemically, also the material appears to be highly stable. As the results indicate only a negligible amount of TA dissolved in various solvents out of the 200 mg taken for its chemical stability in each experiment. The tin(IV) antimonate prepared earlier by Qureshi et al.[2] seems to inferior in this regard. It appears that the starting material used for the preparation of the ion exchanger plays an important role in determining its properties. In the earlier studies antimony(V) chloride was used for synthesizing the material as against the potassium antimonate [$KSb(OH)_6$] used in the present study. No definite conclusion can, however, be drawn at the moment

Table 2. Some Binary Separations of Metal Ions Achieved on Tin(IV) Antimonate Columns

Sl. No.	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used	Volume of eluant (ml)	Maximum limit of the loading capacity of the column/μg
1	Al(III)–Pb(II)	155.3 (Al)	155.3 (Al)	0.00	1 M HNO_3	40	Pb —20721.00
		5698.2 (Pb)	Not leached (Pb)	—	—	—	Al — 809.40
2	Mg(II)–Pb(II)	224.96 (Mg)	218.88 (Mg)	−2.70	0.1 M $HClO_4$	50	Fe — 2513.25
		5698.2 (Pb)	Not leached (Pb)	—	—	—	Mg— 1216.00
3	Fe(III)–Pb(II)	558.5 (Fe)	572.46 (Fe)	+2.49	2 M HCl+2 M NH_4Cl	30	
		5698.2 (Pb)	Not leached (Pb)	—	—	—	
4	Al(III)–Fe(III)	155.3 (Al)	162.0 (Al)	+4.31	1 M HNO_3	50	
		558.5 (Fe)	530.6 (Fe)	−2.55	2 M HCl+2 M NH_4Cl	40	
5	Mg(II)–Al(III)	224.96 (Mg)	218.88 (Mg)	−2.70	0.1 M $HClO_4$	60	
		114.58 (Al)	114.58 (Al)	0.00	1 M HNO_3	50	
6	Mg(II)–Fe(III)	231.04 (Mg)	218.88 (Mg)	−5.26	0.1 M $HClO_4$	60	
		558.5 (Fe)	558.5 (Fe)	0.00	2 M HCl+2 M NH_4Cl	40	

because of the confusing and contradictory statements regarding the varying water contents in the antimonic acid produced on the surface of the material depending upon the starting antimony salt.[15]

The column elution experiments indicate a dependence of the concentration of the eluant on the rate of elution. The minimum molar concentration of $NaNO_3$ as eluant is 1 M for the maximum elution of H^+ ions from a column of 1 g of TA. The elution is quite fast as only 110 ml of the effluent is sufficient for almost complete elution of the H^+ ions from its column.

pH titration curves obtained under equilibrium conditions are shown in Fig. 1 for LiOH/LiCl, NaOH/NaCl, KOH/KCl, and $Ca(OH)_2/CaCl_2$ systems. These studies are different from others generally made on such materials. The normal practice has been to perform the pH-titration under a nonequilibrium process.[2] As it is clear from the figure, the inflection point for the exchange of alkali metals resemble with the i.e.c. obtained, i.e. 2.4 mequiv/dry g. The pH titration curve for Ca^{2+} however does not show any inflection. In this regard our product is similar to antimony(V) silicate[16] and hydrated antimony oxides.[17]

Thermogravimetry and IR studies point to the following tentative formula of the compound

$$Sn_2[Sb(OH)_6]_{11}\cdot nH_2O$$

Assuming that at 100 °C only the external water molecules are lost, the 5.2% loss represented by the TGA curve must be due to the loss of nH_2O from the above structure. The value of 'n', the external water molecules, can be calculated using Alberti's equation:[18]

$$18n = \frac{x(M + 18n)}{100}$$

where, x is the % weight loss (5.2%) in the exchanger on heating upto 100 °C. M=molecular weight of the material minus the external water molecules.

The above equation then gives the external water molecules per molecule of tin(IV) antimonate as ca. 8.

The differential thermogram (DTG) gives a better view of the changes corresponding to the two inflections in the TGA curve (Fig. 3). The sharp peak at ca. 100 °C represents the loss of external water molecules while the other broad one is due to the condensation process which continues upto ca. 500 °C. Beyond this temperature the material might have completely changed into the oxides that is why no further weight loss occurs.

The IR studies confirm the presence of –OH groups and external water molecules in addition to the metal oxides (SnO and Sb_2O_5) present in the material.[19] The

peaks at 1400—1500 cm^{-1} and ca. 3000 cm^{-1} are representative of the external water molecules, the former being also representative of the strongly bonded OH groups in the matrix. As Fig. 2 indicates these peaks are observed even when the material is heated at a much high temperature. It may be due to the absorption of water molecules from the atmosphere by the material during cooling. X-Ray studies point to the amorphous nature of the TA as no peaks are observed by the diffraction pattern.

The most promising property of the material is its extraordinary high selectivity for lead. When the separation of lead from other metal ions was tried on its column, it was observed that lead was totally adsorbed and its leaching was not possible even in an eluant consisting of 4 M HCl + 4 M KCl. It may be due to the formation of an insoluble lead antimonate on the surface. Lead antimonate has been found to an inorganic ion exchanger.[20] The experimental details of some representative separations of Pb(II) from Al(III), Fe(III), and Mg(II) are given in Table 2. Thus, the material can be utilized for a quantitative separation of lead from the mixtures containing several metal ions. This property of TA may prove useful in the environmental studies. Other binary separations tried on the TA column have been Al(III)-Fe(III), Al(III)-Mg(II), and Mg(II)-Fe(III). Table 2 and Fig. 4 illustrate the salient features of these separations.

Conclusion

Tin(IV) antimonate, prepared in these studies as a new inorganic ion-exchange material has a good ion exchange capacity and is highly selective for Pb. This behavior of TA is promising in the field of pollution chemistry where an effective separation method is needed for lead from other pollutants. This material has been characterized on the basis of its chemical and thermal analysis, IR studies, and some ion-exchange characteristics such as ion-exchange capacity, elution and concentration behavior, pH-titrations and distribution studies. On the basis of distribution studies some binary metal separations have been achieved.

The authors thank Prof. K. T. Nasim for the research facilities and the U. P. C. S. T. for the financial assistance to one of them (U. G.).

References

1) "Inorganic Ion Exchange Materials," ed by A. Clearfield, C. R. C. Press Inc., Boca Raton Florida (1982).
2) M. Qureshi, V. Kumar, and N. Zehra, *J. Chromatogr.*, **67**, 351 (1972).
3) M. Qureshi and J. P. Rawat, *J. Inorg. Nucl. Chem.*, **30**, 305 (1968).
4) M. Qureshi, A. P. Gupta, S. N. A. Rizvi, and N. A. Shakeel, *React. Polym. Ion Exch. Solvents*, 3(1), 23 (1984).
5) G. Alberti, U. Costantino, F. DiGregorio, and E. Torracca, *J. Inorg. Nucl. Chem.*, **26**, 2241 (1964).
6) S. A. Nabi and W. A. Siddiqui, *Bull. Chem. Soc. Jpn.*, **59**, 2003 (1986).
7) K. G. Varshney and A. A. Khan, *J. Inorg. Nucl. Chem.*, **41**, 241 (1979).
8) M. Qureshi, K. G. Varshney, and A. H. Israili, *J. Chromatogr.*, **59**, 141 (1971).
9) M. Qureshi, K. G. Varshney, and F. Khan, *J. Chromatogr.*, **118**, 167 (1976).
10) M. Qureshi, R. Kumar, and R. C. Kaushik, *Sepn. Sci. Technol.*, **13**, 185 (1978).
11) I. M. Kolthoff, P. J. Elving, and E. B. Sandell, "Treatise on Analytical Chemistry," Interscience, New York (1961), Vol. 3, Part II, p. 358.
12) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York (1959), Vol. III, p. 266.
13) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, 1949, 3299. 3299 (1949).
14) C. N. Reilly, R. W. Schmidt, and F. S. Sadek, *J. Chem. Educ.*, **36**, 555 (1959).
15) "Inorganic Ion Exchange Materials," ed by A. Clearfield, C. R. C. Press Inc. Boca Raton Florida (1982), p. 197.
16) K. G. Varshney, U. Sharma, S. Rani, and A. Premadas, *Sepn. Sci. Technol.*, **17**, 1527 (1982—83).
17) M. Abe and T. Ito, *Bull. Chem. Soc. Jpn.*, **41**, 333 (1968).
18) G. Alberti, E. Torracca, and A. Conte, *J. Inorg. Nucl. Chem.*, **28**, 607 (1966).
19) C. N. R. Rao, "Chemical Application of Infrared Spectroscopy," Academic Press, New York (1963).
20) P. S. Thind and T. K. Bindal, *J. Liquid Chromatogr.*, **3**, 573 (1980).

J. inorg. nucl. Chem., 1977, Vol. 39, pp. 2075–2078. Pergamon Press. Printed in Great Britain

28

2.2 AMINE Sn(II) HEXACYANOFERRATE(II) AS AN INORGANIC ION-EXCHANGER

K. G. VARSHNEY and SAMEEM NAHEED
Chemistry Section, Z. H. Engng College, Aligarh Muslim University, Aligarh 202001, India

(*Received* 17 *November* 1976; *received for publication* 10 *February* 1977)

Abstract—Thirteen samples of amine hexacyanoferrate(II) compounds of Sn(II) have been prepared using different amines and different mixing ratios of Sn(II) and $Fe(CN)_6^{4-}$. The samples have been analyzed for their composition, ion-exchange capacity and stability in different solvents. Ion-exchange capacity of a number of samples has been determined after drying them at different temperatures and is discussed. IR spectra of the samples containing aniline, piperidine, ethylamine and pyrrole have also been given.

INTRODUCTION

Ammonium hexacyanoferrate(II) compound of cobalt was first synthesized by Petrow and Levine[1], by substituting the ammonium ion for the potassium ion in potassium cobalt(II) hexacyanoferrate(II) which was produced by Prout, Russell and Groh[2]. Later on Hahn and Klein[3] introduced amines in place of ammonium ion and reported that the amine compounds have excellent exchange properties for ^{137}Cs. In these laboratories we have earlier synthesized stannous and stannic ferrocyanides[4, 5] and have explored their ion-exchange potentialities by achieving some separations of metal ions. In continuation, the present study summarizes our efforts to explore some of the characteristics of the amine hexacyanoferrate(II) compounds of Sn(II). The samples thus prepared have been analyzed for their composition, ion-exchange capacity and stability in different solvents. The IR spectra of some of the samples have been discussed.

EXPERIMENTAL AND RESULTS

Reagents and chemicals. Stannous chloride dihydrate and potassium ferrocyanide were obtained from BDH (AnalaR) England. Other reagents and chemicals were of AnalaR grade. Ferrocyanic acid was produced by passing solution of $K_4Fe(CN)_6$ over a bed of Dowex-50W × 8 or Amberlite IR 120 resin in H^+ form.

Synthesis, ion-exchange capacity and stability. 100 ml of 0.1 M solution of $K_4Fe(CN)_6$ were passed through a column of the resin in H^+ form with very slow rate. The column was washed with distilled H_2O and the effluent which is bluish green [$H_4Fe(CN)_6$] was diluted to 250 ml with distilled H_2O. 5 ml of selected amine was added to this solution to form the amine hydrogen salt [$A_2H_2Fe(CN)_6$]. This solution was poured into $SnCl_2$– solution (in 4 M HCl) with stirring. The ppt. thus formed were digested at room temperature for 24 hr before filtering through a vacuum pump and washing several times with demineralized water until the pH of washing became 6 to 7. This material was dried in oven at 60°C and was placed in demineralized water to crack them into small granules. These particles were washed again with water to remove the fine particles in suspension by decantation. They were finally dipped in dil HNO_3 (1 to 2 M); the supernatent acid solution was replaced time to time to ensure complete conversion of the granules into H^+ form. They were then washed with demineralized water to pH 6 and dried material was usually black but blue-green or green granules were also obtained depending on the type of the amine. The pH of the mixed solution was ≈0.

Ion-exchange capacity of the different samples was determined by the column process as usual with 1 M KNO_3 solution. Table 2 summarizes the synthesis and the ion-exchange capacity of different samples prepared.

Based on the ion-exchange capacity four samples (S-6, S-9, S-11, S-13) were selected for other studies. The stability of these samples were usually checked in different acids and bases and it was noticed that nitric acid up to 8 M, hydrochloric acid up to 4 M and sulphuric acid up to 3 M do not effect the granules of these samples even after 24 hr keeping at room temperature. Similarly 0.5 M NaOH and 1 M NH_4OH have no effect on these samples. A quantitative study of the solubility of these samples was made by

Table 1. Synthesis and ion-exchange capacity of different amine based inorganic ion-exchangers

S No.	Vol of 0.1 M $SnCl_2$	Vol of 0.1 M $K_4Fe(CN)_6$	Final vol of $H_4Fe(CN)_6$	Amine added	I.E.C.
1	200 ml	100 ml	250 ml	Dimethylamine	0.64
2	50 ml	100 ml	250 ml	Dimethylamine	0.740
3	200 ml	100 ml	250 ml	Anthranol	0.56
4	50 ml	100 ml	250 ml	Anthranol	0.48
5	200 ml	100 ml	250 ml	Aniline	0.935
6	50 ml	100 ml	250 ml	Aniline	1.170
7	50 ml	100 ml	250 ml	1,3-Diaminopropane	0.54
8	200 ml	100 ml	250 ml	Piperidine	0.905
9	50 ml	100 ml	250 ml	Piperidine	1.44
10	200 ml	100 ml	250 ml	Ethylamine	0.435
11	50 ml	100 ml	250 ml	Ethylamine	1.18
12	200 ml	100 ml	250 ml	Pyrrole	0.74
13	50 ml	100 ml	250 ml	Pyrrole	1.40

Table 2 Solubility of samples S-6, S-9, S-11 and S 13 in different solvents

Solvent	Solubility (mg/50 ml)							
	Sample S 6		Sample S 9		Sample S 11		Sample S 13	
	Fe	Sn	Fe	Sn	Fe	Sn	Fe	Sn
1 *Distilled water*	*0 102*	*0 20*	*0 150*	*0 150*	0 20	0 25	0 40	0 30
2 0 05 M HNO_3	0 25	0 00	0 28	0 30	0 20	0 30	0 60	0 50
3 0 5 M HNO_3	0 20	0 10	0 25	0 25	0 25	0 35	0 50	0 45
4 1 0 M HNO_3	0 40	0 15	0 30	0 50	0 30	0 40	0 70	0 50
5 2 0 M HNO_3	0 40	0 15	0 35	0 40	0 25	0 60	0 60	0 50
6 4 0 M HNO_3	10 0	5 00	15 00	10 00	15 00	7 50	17 50	15 0
7 4 0 M HCl	18 00	20 00	17 75	18 00	15 75	18 0	17 60	15 75
8 3 M H_2SO_4	20 00	22 50	20 00	17 50	21 00	22 50	20 25	18 75
9 5% NH_2OH HCl	0 20	0 105	0 30	0 25	0 20	0 40	0 25	0 20
10 10% Hydrazine sulphate	0 13	0 50	0 20	0 40	0 20	0 25	0 40	0 45
11 10% Ascorbic acid	0 125	0 25	0 25	0 30	0 50	0 30	0 50	0 80
12 1% Tartaric acid	0 125	0 25	0 30	0 25	0 45	0 75	0 50	0 75
13 *1% Oxalic acid*	*0 130*	*0 25*	*0 50*	*0 75*	*0 40*	*0 80*	*0 75*	*0 75*
14 1 M $K_4Fe(CN)_6$	Complete dissolution							
15 1% Na_2SO_3	Complete dissolution							
16 1% Na_2CO_3	Complete dissolution							

shaking 500 mg of the exchanger in 50 ml each of a large number of solvents at room temperature (30±2°) for 6 hr to attain equilibrium and then chemically analyzing the solutions, by the standard procedures[4] Table 2 summarizes the results obtained

Thermal stability Thermal ion-exchange capacities were determined at different drying temperatures For this purpose one gram each of the samples was kept at different temperatures for 1 hr each After cooling to room temperature their ion-exchange capacity was determined as usual. Table 3 shows the results of this study

Composition 200 mg of exchanger were heated with 10 ml of H_2SO_4 and 50 ml of HCl The colour of the solution was blue turning to yellow It was cooled and stannous chloride solution (60 g $SnCl_2$ in 600 ml HCl and 400 ml H_2O) was added dropwise to the cold solution until the colour of iron was no longer evident (yellow colour disappears) The excess of $SnCl_2$ was destroyed with mercuric chloride (saturated solution) as usual Fifteen milliliters of phosphoric acid–sulphuric acid mixture (150 ml H_3PO_4 + 150 ml H_2SO_4 diluted to 1000 ml) were then added and the volume was made up to 200 ml with distilled water Iron was determined by titration against a $K_2Cr_2O_7$ solution using diphenyl amine as indicator[6] For the simultaneous determination of tin and iron in the exchanger 200 mg were dissolved in sulphuric acid and HCl mixture as above 10 ml of conc H_2SO_4 100 ml of conc HCl and about 2 to 3 g of test lead in a 500 ml of conical flask were added to the solution The volume was made up to 300 ml with distilled H_2O and the solution was heated for an hour in an atmosphere of CO_2 It was then cooled to 10°C in an ice bath Tin and iron in the reduced state were titrated against 0 1 N $K_2Cr_2O_7$ using diphenyl amine as indicator The total quantity of tin and iron in the exchanger was thus determined The amount of tin was then obtained by subtracting the quantity of iron from the total amount of tin and iron The results are summarized in Table 4

Table 3. Ion-exchange capacity of the different samples at different drying temperatures

Drying temp	Samples	Ion-exchange capacity	Color of exchanger
60°C	S-6	1 2	Blue-black
	S-9	1 44	Blue-black
	S-11	1 18	Blue-black
	S-13	1 4	Blue-black
100°C	S-6	1 2	Dirty-black
	S-9	1 30	Dirty-black
	S-11	1 1	Dirty black
	S-13	1 3	Dirty-black
200°C	S-6	0 80	Brownish black
	S-9	0 88	Brownish black
	S-11	0 15	Brownish black
	S-13	0 80	Brownish black
400°C	S-6	0 1	Light brown
	S-9	0 5	Light brown
	S-11	0 05	Light brown
	S-13	0 1	Light brown
500°C	S-6	0 00	Deep brown
	S-9	0 00	Deep brown
	S-11	0 00	Deep brown
	S-13	0 00	Deep brown

The amount of amine in the samples was determined by the following procedure

1 g of the exchanger was mixed with 200 ml of 10 M NaOH and the amine distilled into 100 ml of nearly saturated boric acid solution The amount of base thus distilled was determined by titrating the boric acid solution with standard 0 1 M HCl to a bromocresol green end point

IR spectra IR spectra of the samples S-6, S 9, S 10, S 11 and S-13 are shown in Fig 1 drawn by the Nujol method using CsBr window

DISCUSSION

It is clear from the results that amine tin(II) hexa cyanoferrate(II) compounds are fairly stable They are as stable as stannous ferrocyanide itself for the dissolution of Sn and Fe in different solvents such as distilled water, HNO_3, HCl and H_2SO_4 Other reducing agents like hydroxyl amine hydrochloride, hydrazine sulphate, ascorbic acid and tartaric acid have negligible effect on these materials However, $K_4Fe(CN)_6$, Na_2SO_3 and Na_2CO_3 dissolved them completely

The ion-exchange capacity of these materials is lower in comparison to stannous ferrocyanide The structural formula proposed for stannous ferrocyanide[4] has been $[SnO\ H_4Fe(CN)_6\ 2\ 5H_2O]_n$, and its ion-exchange capacity was reported to be 2 03 m eq/g dry weight of the exchanger During the preparation of amine salts, the selected amine is first mixed with $H_4Fe(CN)_6$ thus forming an amine hydrogen salt $[A_2H_2Fe(CN)_6]$ which may *finally form the product as* $[SnO\ A_2H_2Fe(CN)_6]_n$ This formula is in accordance with the composition of the

Table 4 Composition of amine Sn(II) hexacyanoferrate(II) compounds

Sample No	Weight of the exchanger	Vol of 0 1 N $K_2Cr_2O_7$ used for iron (ml) (a)	Vol of 0 1 N $K_2Cr_2O_7$ used for iron and tin (ml) (b)	Vol of 0 1 N $K_2Cr_2O_7$ used for tin only (ml) ($b-a$)	Molar ratio Sn Fe $\frac{(b-a)}{2}$ a
S 6	200	5	15	10	1 1
	200	5 5	16 25	10 75	1 1 03
S 9	200	4 5	15 00	10 5	1 0 87
	200	4 75	15 00	10 25	1 0 93
S 11	200	5 2	15 5	10 3	1 1
	200	5 5	16 00	10 5	1 1 04
S 13	200	5 3	15 6	10 3	1 1 03
	200	5 2	15 3	10 1	1 1 03

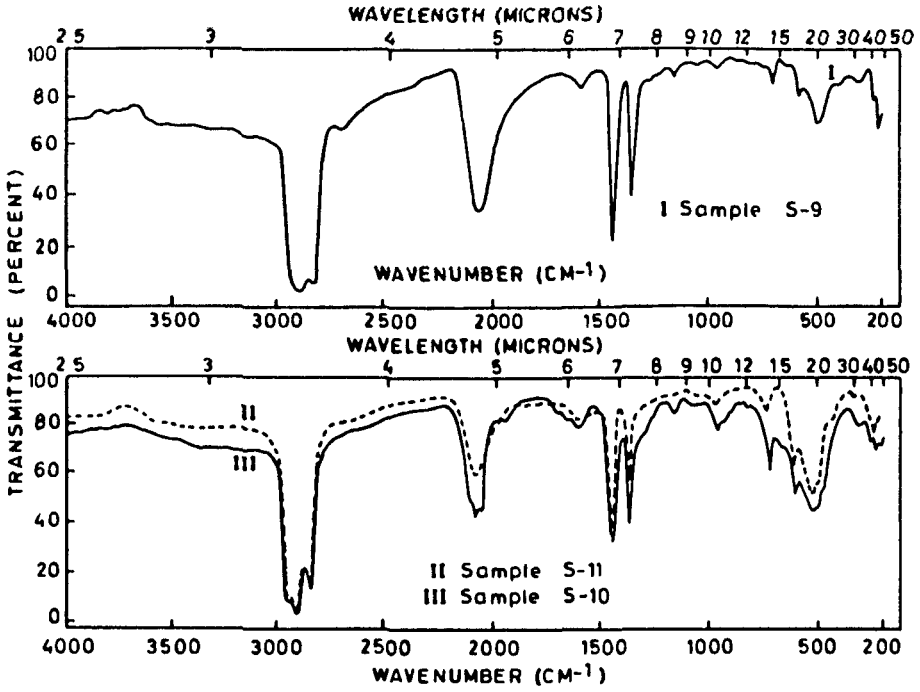


Fig 1 IR spectra of amine hexacyanoferrate(II) ion exchangers

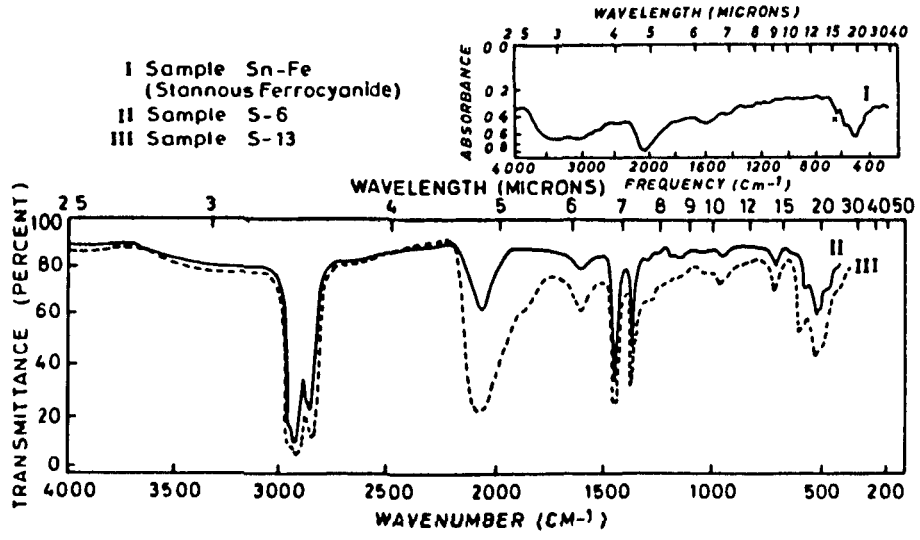


Fig 2 IR spectra of amine hexacyanoferrate(II) ion-exchangers

compounds determined (Table 4). It is apparent that number of exchangeable H^+ ions are now less than in stannous ferrocyanide, thereby, reducing the ion-exchange capacity. Thus the highest value of ion-exchange capacity is obtained in a sample prepared with piperidine or pyrrole while the least ion-exchange capacity is observed in a compound containing anthranol. All the seven amines used in these studies can be put in following order based on the ion-exchange capacity of ferrocyanide containing them.

Piperidine = pyrrole > aniline = ethylamine > dimethylamine > 1,3-diaminopropane > anthranol.

Further studies are, however, needed before some definite conclusions may be drawn regarding the fall of ion-exchange capacity with the variation of these amines. In all cases the ion-exchange capacity is enhanced if the amount of $Fe(CN)_6^{4-}$ relative of Sn(II) is increased (Table 1).

Drying temperature also has an impact on ion-exchange capacity of the sample (Table 3). The ion-exchange capacity of the sample dried at 60°C and of the one dried at 100°C, remained almost the same which indicates that on heating up to 100°C no structural changes take place, only the colour of the material changes from blue black to dirty black. The samples lose their ion-exchange capacity to an appreciable extent when heated up to 200°C, evidently because now the water molecules are lost due to the condensation of the structure thereby losing the replaceable H^+ ions. On further heating, say up to 400°C the ion-exchange capacity is almost completely lost by all the samples except sample No. S-9 (piperidine compound) which retains it as 0.5 m eq/dry g. It may be due to the completion of condensation process in the ion-exchangers—a drying temperature more than 400°C gives all the samples deep brown colour, probably because now the materials are completely converted into the oxides of tin and iron. The IR spectra of the samples S-6, S-9, S-10, S-11 and S-13 along with the one for stannous ferrocyanide (Figs. 1 and 2) show a distinction between these samples and stannous ferrocyanide alone. For stannous ferrocyanide we observe the peaks at ~500, 600, 1610, 2100 and 3000 cm^{-1}, which are also shown by the amine ferrocyanides thus confirming the presence of SnO (~500 cm^{-1}), M–C stretching in $Fe(CN)_6^{4-}$ (600 cm^{-1}) water molecules (1610 and 3000 cm^{-1}), and ferrocyanide groups (~2100 cm^{-1}). The presence of additional peaks in the amine compounds can be interpreted as follows.

Frequency range	Nature of the peak	Interpretation
725 cm^{-1}	Sharp, weak	N-H rocking frequency
980 cm^{-1}	Diffuse; weak	C-H rocking frequency
1380 cm^{-1}	V.sharp; V.strong	OH- bending frequency and due to the presence of CH_3- or CH_2 groupings
1610 cm^{-1}	Diffuse; V.weak	N-H bending frequency

Acknowledgement—The authors are grateful to Prof. Mohsin Qureshi for research facilities.

REFERENCES

1. Henry G. Petrow and H. Levine, *Anal. Chem* 39, 360 (1967).
2. W. E. Prout, E. R. Russell and H. J. Groh, *J. Inorg. Nucl. Chem.* 27, 473 (1965).
3. Richard B. Hahn and Henry C. Klein, *Anal. Chem.* 40, 1135 (1968).
4. Mohsin Qureshi, K. G. Varshney and Fahmida Khan, *J. Chromatogr.* 65, 547 (1972).
5. Mohsin Qureshi, K. G. Varshney and A. H. Israili, *J. Chromatogr.* 59, 141 (1971).
6. W. W. Scott, *Standard Methods of Chemical Analysis*. Vol. 1, 5th Edn, p. 473. Van Nostrand, New York (1939).

Indian Journal of Chemistry
Vol. 21A, April 1982, pp. 398-401

2.3 Synthesis & Ion Exchange Properties of Amine Tin(IV) Hexacyanoferrate(II) & Its Use in the Separation of Cadmium(II) from Zinc(II), Manganese(II), Magnesium(II) & Aluminium(III)

K. G. VARSHNEY*, ASIF A. KHAN & S. S. VARSHNEY†
Chemistry Section, Z. H. College of Engineering & Technology, Aligarh Muslim University, Aligarh 202 001

Received 27 *June* 1981; *revised and accepted* 16 *November* 1981

A new type of inorganic ion exchanger, amine Sn(IV) hexacyanoferrate(II), with seven different amines has been prepared. Different samples of the exchanger have been prepared to study the ion exchange capacities for different metals at different temperatures. Based on *p*H titrations, elution curves, IR and thermogravimetric studies, a tentative formula of the compound has been proposed. The utility of this material has been tested by achieving some important binary metal separations such as Cd^{2+} -Zn^{2+} and Cu^{2+} -Al^{3+}.

METAL hexacyanoferrates(II) have been used as scavengers for the removal of alkali metals from sea water, milk and urine[1-4]. Ammonium hexacyanocobaltferrate(II) was reported to have an extra affinity[5] for Cs and was found to be useful for the analysis of ^{137}Cs. A further improvement in its performance was achieved[6] using a high molecular weight amine instead of NH_4^+ ions in its preparation. In continuation of the earlier work[7-9] from our laboratories on Sn(II) and Sn(IV) hexacyanoferrates(II) and amine Sn(II) hexacyanoferrate(II) as ion exchangers, we have now prepared amine Sn(IV) hexacyanoferrate(II). Some important binary metal separations, such as Cd^{2+} from Zn^{2+}, Mn^{2+}, Mg^{2+} and Al^{3+} and Cu^{2+} from Al^{3+} have been achieved using this ion exchanger.

Materials and Methods

Stannic chloride (p.p.H. Polskie Odczynniki chemiczene gliwice, Poland) and potassium hexacyanoferrate (II) (BDH, England) were used. Other reagents and chemicals were of AR grade. Ferrocyanic acid was obtained by passing a solution of $K_4Fe(CN)_6$ over a bed of Amberlite IR-120 resin in H^+ form.

*p*H-metric and IR studies were carried out using Elico digital model LI-120 *p*H meter and Perkin-Elmer model 137 spectrophotometer respectively. TGA studies were made on a thermo-balance designed by FCI (Sindri). For X-ray studies, a Philips X-ray unit with Ni-filtered Cu-K_α radiations was used. SEM studies were made on a Cambridge Stereoscan Electron Microscope attached with an X-ray Microprobe Analyser.

Synthesis — $K_4Fe(CN)_6$ solution (100 ml, 0.1*M*) was passed through a resin column in H^+ form with a very slow rate. The column was washed with distilled water so that the effluent, bluish-green in colour, was approximately 275 ml in volume. An excess of the selected amine (~5 ml) was added to this solution to prepare the amine hydrogen salt $[A_2H_2Fe(CN)_6]$. Hydrazine sulphate was taken as solid (1 g). This solution was poured into a 0.1*M* stannic chloride solution dropwise, stirring rapidly. Conc. HCl was added to maintain the *p*H around 1. The precipitate thus formed was kept at room temperature for 24 hr before filtering *in vacuo*. The precipitate was washed several times with demineralized water (DMW) until the *p*H of washing became 5-6. The material was finally dried in an oven at 50°C and cracked into small granules by immersing it in DMW. It was converted into the H^+ form by putting it in 1-2*M* HNO_3. The excess acid was washed out and the material was again dried in air at 50°C. Different samples were prepared by varying the volume of the $SnCl_4$ solution. Ion exchange capacity (i.e.c.) of different samples was determined by the column process using 1.0*M* KNO_3 solution. The results are summarized in Table 1. On the basis of its better exchange capacity, lower solubility and higher yield as compared to other samples prepared, sample S-2 was selected for a detailed study.

Results and Discussion

The composition of the exchanger was determined by the same procedure as adopted earlier[9] for amine Sn(II) hexacyanoferrate (II). The amounts of tin and iron, determined by the standard methods[10,11], were found to be 33% and 18% respectively in the substance.

As the material was a cation exchanger, its i.e.c. was found using 1.0 to 2.0*M* solutions of metal ions (alkali and alkaline earth metal ions), by the column process as usual[9]. Since the concentration of the eluant was found to affect the elution behaviour of the material, KNO_3 solutions (200 ml) of

†Department of Chemistry, Hindu College, Moradabad 244 001.

TABLE 1 — SYNTHESIS AND ION EXCHANGE CAPACITIES OF DIFFERENT AMINE BASED Sn(IV) HEXACYANOFERRATES(II)

Sample No.	Volume of 0.1*M* $SnCl_4$ (ml)	Amine added	i.e.c. meq/g (dry)
S-1	50	Aniline	1.86
S-2	200	Do	1.70
S-3	100	Do	1.60
S-4	300	Do	1.20
S-5	50	Ethyl amine	1.65
S-6	200	Do	1.62
S-7	50	Diethanolamine	1.20
S-8	200	Do	1.03
S-9	50	Hydrazine sulphate	1.14
S-10	200	Do	0.91
S-11	50	Methyl amine	1.30
S-12	200	Do	1.23
S-13	50	Dimethyl amine	1.05
S-14	200	Do	1.00
S-15	50	Ethanolamine	0.72
S-16	200	Do	0.58

varying concentrations (0.1 to 2.5*M*) were passed through the column bed of 0.5 g material. The maximum i.e.c. was obtained with an eluant concentration of ~2.0*M*. Also, approximately 130 ml of the eluant were enough for the complete elution of H^+ ions from the column. The ion exchange capacity (meq/g) of sample S-2 for different metal ions (hydrated radii, Å in parentheses) is as follows : Li^+ (3.40), 1.01; Na^+ (2.76), 1.15; K^+ (2.32), 1.70; Rb^+ (2.28), 1.06; Cs^+ (2.28), 1.20; Mg^{2+} (3.10), 0.52; Ca^{2+} (2.00), 1.10; Sr^{2+} (1.80), 0.90; and Ba^{2+} (1.50), 0.86. On heating 1.0 g of the exchanger at various temperatures for 1 hr the i.e.c. was observed to decrease. It became 0.30 meq/g on heating the substance upto 150°C, 0.08 meq/g on heating it upto 200°C and almost zero beyond this temperature.

Solutions of LiOH, NaOH and KOH containing different amounts of OH^- were taken and the exchanger (500 mg) was added to each solution. The common ion effect was nullified by adding respectively metal salts (LiCl, NaCl and KCl), keeping the total volume 50 ml. After allowing the solutions to stand for 24 hr for the attainment of equilibrium, the *p*H was recorded and plotted against the OH^- added (Fig. 1).

Distribution studies — The distribution coefficients (K_d) of 14 metal ions for sample S-2 were determined as usual[9] by the batch process in DMW and $10^{-2}M$ HNO_3 solutions. The metal ions were determined in the solution volumetrically[12] using EDTA. The following formula was used for determining K_d values,

$$K_d = \frac{I-F}{F} \times \frac{V}{M} \text{ ml g}^{-1}$$

where I = initial concentration of the metal in solution, F = final concentration of the metal after equilibrium, V = total volume of the solution (ml) and M = weight of the exchanger (g). The K_d values obtained are shown in Table 2.

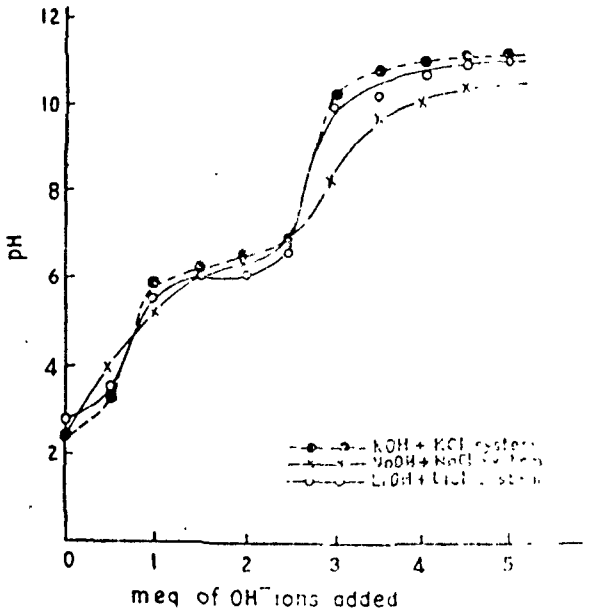


Fig. 1 — *p*H titration curves for sample S-2.

TABLE 2 — DISTRIBUTION COEFFICIENTS OF SOME METAL IONS ON SAMPLE S-2

Metal ions	K_d (ml/g) in	
	DMW	$10^{-2}M$ HNO_3
Ba^{2+}	85.0	40.0
Sr^{2+}	85.0	14.0
Ca^{2+}	175 × 10^3	0.0
Zn^{2+}	55.0	46.0
Mn^{2+}	0.0	0.0
Mg^{2+}	25.0	0.0
Cd^{2+}	43.8 × 10^3	1.02 × 10^3
Al^{3+}	60.0	0.0
Hg^{2+}	6.00 × 10^3	5.62 × 10^3
Cu^{2+}	43.8 × 10^3	1.01 × 10^3
La^{3+}	3.62 × 10^3	3.62 × 10^3
Pr^{3+}	68.0	68.0
Th^{4+}	7.00 × 10^3	2.38 × 10^3
Bi^{3+}	16.5 × 10^3	9.75 × 10^3

Separations achieved — Table 3 shows the binary separations achieved using 1 g columns of this exchanger, with all the details of amounts of the metal ions loaded and recovered alongwith the % error in each case.

Different samples of the amine Sn(IV) hexacyanoferrate(II) exchanger (Table 1) show reproducible stoichiometry, water content and ion exchange capacity. The i.e.c. appears to depend on the nature of the amine used in the preparation of the exchanger. It varies in the following order : aniline > ethyl amine > methyl amine > diethylamine > hydrazine sulphate > dimethylamine > ethanolamine. The same order was observed in the case of amine Sn(II) hexacyanoferrate (II) exchanger prepared earlier[9].

On the basis of chemical analysis, TGA and IR studies the following formula may be tentatively proposed for the compound :

$[Sn(OH)_4.A_2.H_2Fe(CN)_6]n.H_2O$, $A = C_6H_5NH_3^+$

TABLE 3 — QUANTITATIVE SEPARATION OF METAL IONS ON COLUMNS OF SAMPLE S-2

Separation achieved	Metal ion eluted	Amount loaded (μg)	Amount recovered (μg)	Eluant	Error (%)
Zn^{2+}-Cd^{2+}	Zn^{2+}	305.5	299.0	0.02*M* NH_4NO_3	−2.1
	Cd^{2+}	241.9	247.6	4*M* HNO_3 in 2*M* NH_4NO_3	+2.4
Mn^{2+}-Cd^{2+}	Mn^{2+}	264.0	269.5	0.02*M* NH_4NO_3	+2.03
	Cd^{2+}	241.9	247.6	4*M* HNO_3 in 2*M* NH_4NO_3	+2.4
Mg^{2+}-Cd^{2+}	Mg^{2+}	100.8	105.6	0.02*M* NH_4NO_3	+4.7
	Cd^{2+}	241.9	245.3	4*M* HNO_3 in 2*M* NH_4NO_3	−1.4
Al^{3+}-Cd^{2+}	Al^{3+}	94.5	102.6	0.02*M* NH_4NO_3	+8.6
	Cd^{2+}	241.9	247.6	4*M* HNO_3 in 2*M* NH_4NO_3	+2.4
Al^{3+}-Cu^{2+}	Al^{3+}	94.5	89.1	0.02*M* NH_4NO_3	−5.5
	Cu^{2+}	137.2	145.8	4*M* HNO_3 in 2*M* NH_4NO_3	+6.3

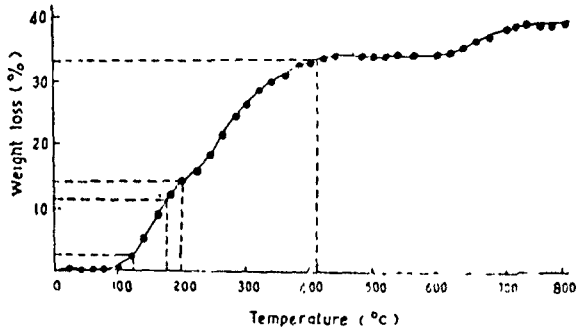


Fig. 2 — Thermogram for Sn (IV) aniline hexacyanoferrate(II) in H^+ form.

The stoichiometry of $A_2H_2Fe(CN)_6$ has earlier been established[6]. The number of external water molecules, *n*, was determined from the thermogram of the sample S-2 (Fig. 2) using Alberti's formula,

$$18n = \frac{x\ (M + 18n)}{100}$$

where x = % weight loss in exchanger, n = number of external water molecules and M = molecular weight of the exchanger without water molecules.

If it is assumed that all external water is removed at 200°C, which corresponds to a weight loss of ~14%, the value of *n* comes out to be 5.3. A further loss in weight upto 410°C may be accounted for by the loss of internal water molecules and cyanogen which comes off[13] at 237°C. Beyond 410°C the weight of the exchanger becomes constant upto 600°C. A loss in weight between 600° and 700°C may be due to the removal of C as CO_2. Above this temperature only the oxides of tin and iron are left as indicated by the grey colour of the residue.

The *p*H titration curves (Fig. 1) indicate that the compound exhibits two end points with a combined exchange capacity of ~6 meq/g corresponding to a 4 meq/mol of the exchanger. The first end point corresponds to an i.e.c. of ~2 meq/g (~ 1meq/mol). It is probably due to the release of one H^+ from the $H_2Fe(CN)_6$ site. During the second end point the remaining H^+ ion of this site and two more H^+ ions from a more basic site, $Sn(OH)_4$, might be released, giving a total ion exchange capacity of 4 meq/mol.

The IR spectra of the first four samples (S-1, S-2, S-3 and S-4) dried at 50°C show peaks at ~500, ~600, ~800, ~980, ~1400, ~1610, ~2100 and ~3000 cm^{-1}. Some of these confirm the presence of SnO (~500), M-C stretching in $Fe(CN)_6^{4-}$ ~(600), water molecules (~1610 and 3000 cm^{-1}) and ferrocyanide group (~2100 cm^{-1}) The rest are observed due to the presence of N-H rocking mode (~725 cm^{-1}), CH rocking mode (~980 cm^{-1}) and O-H bending mode (~1640 cm^{-1}). The OH bands at ~3000 cm^{-1} are indicative of strongly hydrogen bonded OH or extremely strongly coordinated H_2O. The IR spectra obtained for the samples dried at different temperatures i.e. at 100°, 150°, 200° and 400° show a gradual decrease in the intensities of peaks at 2100 cm^{-1} and 1610 cm^{-1}. This is because of the loss of CN^- and H_2O molecules on heating. The intensity of the peak at 3000 cm^{-1} is also affected because of the condensation of the exchanger molecule which is accompanied by the removal of strongly coordinated H_2O molecules.

The X-ray studies show that the material is essentially amorphous in nature, and this finding is supported by the SEM studies.

The aniline Sn(IV) hexacyanoferrate (II) is found to be highly selective for Cd^{2+} and Cu^{2+} (Table 2). The selectivity for metal ions decreases considerably in acid solutions, which is obvious. On this basis some metal ion separations were tried and actually achieved as summarized in Table 3. Amine Sn(IV) hexacyanoferrate(II), therefore, seems to have higher separation potential than the Sn(II) salt prepared earlier.

Acknowledgement

The authors thank Prof. M. Qureshi for research facilities and Dr (Mrs) G. K. Sandhu of G. N. D. University (Amritsar) for TGA work. The X-ray and SEM studies were carried out at the Hatfield Polytechnic Hertfordshire (U.K.) for which Dr D. V. Nowell is thanked. The financial assistance from the UGC and CSIR, New Delhi is gratefully acknowledged.

References

1. BARTON, G. B., HEPWORTH, J. L., MCCLANAHAN (JR), MOORE, R. L. & TUYL, H. H. V., *Ind. Engng Chem.*, 50 (1958), 212.
2. MISHIO, M., KAMOSHIDA, A., KADOYA, S. & ISHIHARA, T., *J. At. Energy Soc. Japan*, 6 (1964), 2.
3. KOURIM, V., RAIS, J. & MILLION, B., *J. inorg. nucl. Chem.*, 26 (1964), 1111.

4. KOURIM, V. & MILLION, B., *Colln Czech. Chem. Commun.*, 30 (1965), 2848.
5. PETROW, H. G. & LAVINE, H., *Analyt. Chem.*, 39 (1967), 360.
6. HAHN, R. B. & KLEIN, H. C., *Analyt. Chem.*, 40 (1968), 1135.
7. QURESHI, M., VARSHNEY, K. G. & ISRAILI, A. H., *J. Chromatogr.*, 59 (1971), 141.
8. QURESHI, M., VARSHNEY, K. G. & KHAN, F., *J. Chromatogr.*, 65 (1972), 547.
9. VARSHNEY, K. G. & NAHEED, S., *J. inorg. nucl. Chem.*, 39 (1977), 2075.
10. SCOTT, W. W., *Standard methods of chemical analysis*, Vol. I (Interscience, New York), 1939, 433.
11. KOLTHOFF, I. M. & BELCHER, R., *Volumetric analysis*, Vol. III (Interscience, New York), 1957, 321-322.
12. REILLEY, C. N., SCHMID, R. W. & SADEK, F. S., *J. chem. Educ.*, 36 (1959), 555.
13. DUVAL, C., *Inorganic thermogravimetric analysis* (Elsevier New York), 1963, 179.

ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY 17, 000–000 (1989)

2.4

Synthesis, Characterization, and Ion Exchange Behavior of Antimony(V) Phosphate: Selective Adsorption of Cadmium and Mercury on Its Column

K. G. VARSHNEY AND S. M. MAHESHWARI

Analytical Laboratory, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India

Received January 11, 1988

Antimony(V) phosphate has been prepared as a new inorganic ion exchanger suitable for the selective adsorption of cadmium and mercury, the two chief polluting metals. The material possesses good ion exchange capacity and stability, both thermal and chemical. It has also been characterized and an empirical formula has been proposed on the basis of its chemical analysis and certain instrumental studies like infrared spectroscopy, X-rays, thermogravimetry, derivative thermogravimetry, differential thermal analysis, and pH titrations.

Antimony-based inorganic ion exchangers have received attention mainly because of their promising ion exchange behavior and stability (Abe and Ito, 1968; Baltsie and Huys, 1969; Belinskaya *et al.*, 1976; Novikov, 1976). Antimony silicate has shown its utility in the separation of alkaline earths (Varshney *et al.*, 1982–1983; Varshney and Rani, 1983) and in the selective adsorption of pesticides from soil (Varshney *et al.*, 1985). Use of inorganic ion exchangers in the study of water pollution is important in the present context. Industrial effluents from electroplating plants and iron galvanizing plants pollute sources of water with cadmium. Minute amounts of cadmium can give rise to nephrotoxic and cardiovascular changes. It tends to accumulate in the liver, kidneys, and thyroid gland of human beings. Mercury enters water supplies through pollution by effluents from alkali (NaOH) or pesticides (containing mercury) from manufacturing plants. It affects the nervous system. Mercury salts are highly toxic and are a cumulative type of poison. In the authors' search for an inorganic ion exchanger suitable for the removal of pollutants from water, antimony(V) phosphate has been found to be highly selective for cadmium and mercury. The present paper summarizes a systematic study of its synthesis, surface characterization, and analytical utility in the separation of these two metal ions from others.

MATERIALS AND METHODS

Reagents Antimony(V) chloride (Fluka, Switzerland) used in this study was of approximately 98% purity and the trisodium orthophosphate was a BDH (Pool, England) product. All other reagents and chemicals were of analytical reagent grade.

Instrumentation A Beckman IR-20 spectrophotometer was used for the infrared absorption studies while a Bausch and Lomb Spectronic-20 spectrophotometer was used for colorimetry. Atomic absorption studies were made on a Pye-Unicam Model SP-2900 and pH measurements were made on an Elico Model LI-10 pH meter (India). Thermogravimetric analysis was done with the help of a thermobalance consist-

0147-6513/89 $3.00

TABLE 1

SYNTHESIS OF VARIOUS SAMPLES OF ANTIMONY(V) PHOSPHATE AS CATION EXCHANGER

Sample no.	Mixing ratio ($Sb:PO_4$) by volume	Concentration of antimony(V) chloride (M)	Concentration of trisodium orthophosphate (M)	Na-ion exchange capacity (meq/dry g)	Appearance
1	1:1	0.10	0.50	1.60	Glassy
2	1:1	0.10	0.20	1.20	Glassy
3	1:1	0.10	0.05	1.75	Glassy
4	1:1	0.30	0.30	2.00	White powder
5	2:1	0.10	0.20	1.50	White powder
6	1:2	0.05	0.05	1.40	Glassy

ing of a Cahn RG Model 2050 electrobalance and a nichrome wound resistive furnace.

Preparation of the reagent solutions. A stock solution (1.58 M) of antimony(V) chloride ($SbCl_5$) was prepared in 4 M HCl to avoid its hydrolysis. Further dilutions were also made in 4 M HCl. Trisodium orthophosphate ($Na_3PO_4 \cdot 12H_2O$) was dissolved directly in demineralized water (DMW) to prepare its solution of a desired concentration.

Synthesis of the ion exchange material. Various samples of antimony(V) phosphate were prepared by mixing the solutions as reported in Table 1, and adjusting the pH of the resultant mixture in the range 0–1 by adding ammonia (NH_4OH) with constant stirring. The gel thus obtained was kept for 24 hr at room temperature (approx 30°C) and filtered by suction. The excess acid was removed by washing the gel with DMW which was dried in an air oven at 45°C. The dried gel was converted into small granules by its placement in DMW and it was converted into the H^+ form by treatment with approximately 1 M HNO_3 for 24 hr with occasional shaking and intermittent replacement of the supernatant liquid. The material thus obtained was finally washed to a pH 6–7 and dried at 45°C as above. The appearance of the various samples is reported in Table 1. On the basis of its appearance, apparent chemical stability, and Na^+-ion exchange capacity, sample 3 was selected for all further studies. Reproducibility was verified by preparing the sample several times following the same procedure. Particles of a uniform size (60–100 mesh) were obtained by grinding and sieving.

Ion exchange capacity (IEC). The IEC was determined by the usual column process of placing 1 g of the exchanger (60–100 mesh) in a glass tube of approx 1 cm i.d. fitted with glass wool in the bottom, maintaining a slow flow rate (approx 0.5 ml/min) of the eluant (1 M metal solution). The total volume of eluant necessary for complete elution of H^+ ions was found to be approx 250 ml. The H^+ ions thus eluted out were titrated against a standard alkali solution. The IEC (meq/dry g) of the material for various metal solutions were as follows: LiCl (1.81), KCl (1.83), $NaNO_3$ (1.75), NH_4NO_3 (1.56), $Mg(NO_3)_2$ (1.35), $Ca(NO_3)_2$ (1.25).

Composition. Antimony and phosphorus in the exchanger were determined colorimetrically as well as by the atomic absorption spectrophotometric method.

The colorimetric methods were as follows:

TABLE 2

CHEMICAL STABILITY OF ANTIMONY(V) PHOSPHATE IN VARIOUS SOLVENTS

Sample no.	Solvent	Amount dissolved in ppm	
		Antimony	Phosphorus
1.	1 *M* HNO_3	2.41	5.33
2.	2 *M* HNO_3	3.15	6.99
3.	1 *M* $HClO_4$	1.18	2.67
4.	2 *M* $HClO_4$	2.11	3.33
5.	1 *M* HCl	3.33	5.00
6.	2 *M* HCl	3.15	6.67
7.	4 *M* HCl	6.48	18.66
8.	1 *M* H_2SO_4	2.78	7.67
9.	2 *M* H_2SO_4	3.61	13.67
10.	1 *M* CH_3COOH	5.18	9.67
11.	1 *M* $NaNO_3$	0.56	1.33
12.	0.1 M NaOH	2.96	7.00
13.	1.0 *M* NaOH	D.A.[a]	D.A.
14.	0.1 *M* KOH	18.51	49.99
15.	1.0 *M* KOH	D.A.	D.A.
16.	DMW	0.70	0.33

[a] D.A., dissolved appreciably.

Determination of antimony. The exchanger (0.5 g) was dissolved in 20 ml of concentrated HCl by heating. To 2 ml of this solution were added 1.6 ml of 18 *N* H_2SO_4 and 5 ml of KI reagent (11.2 g of KI + 2 g of ascorbic acid in 100 ml water). The color so developed was diluted to 10 ml with water in a standard volumetric flask and the absorbance was measured after 2–3 min at 425 nm against a reagent blank (Sandell, 1959).

Determination of phosphorus. Ten milliliters of the sample solution was mixed with 100 ml of a 0.5 *M* $NaHCO_3$ solution to which was added 1 teaspoon of carbon black or animal charcoal. The mixture was shaken for 30 min on a mechanical shaker and then filtered through Whatman No. 42 filter paper. Fifteen milliliters of the filtrate followed by 5 ml of an ammonium molybdate solution (1.5 g ammonium molybdate + 100 ml of 3.2 *N* HCl + 5 ml of concentrated HCl) was placed in a 25-ml volumetric flask. One milliliter of a $SnCl_2$ solution (10 g $SnCl_2 \cdot 2H_2O$ dissolved in 25 ml of concentrated HCl diluted to 1320 ml with water) was then added and the volume was made up to the mark. The absorbance was recorded at 660 nm against a reagent blank prepared in a similar manner (Olsen, 1954). The molar ratio of Sb and PO_4^{3-} was found to be approximately 4:3.

Chemical stability. An antimony(V) phosphate sample of 250 mg was treated with 25 ml of the various solvents for 24 hr at room temperature with intermittent shaking. Antimony and phosphate were determined in the supernatant liquid colorimetrically by the methods given above. Table 2 summarizes the results.

pH titrations. pH titrations were performed by the method of Topp and Pepper (1949). Five hundred milligrams of the exchanger was placed in each of several 250-

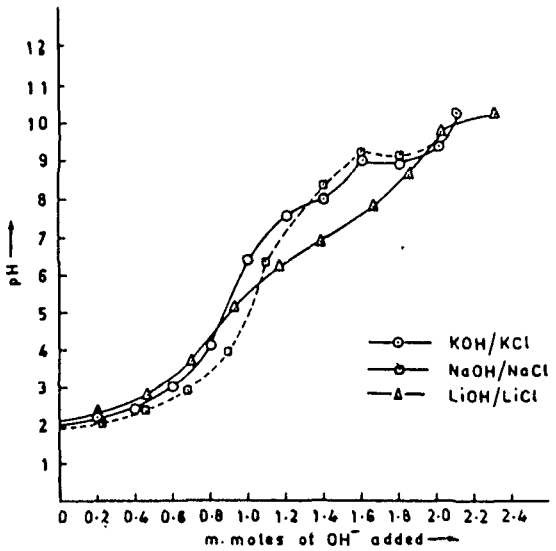


FIG. 1. Equilibrium pH titration curves of antimony(V) phosphate cation exchanger.

ml conical flasks, followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml to maintain constant ionic strength. The pH of the solutions were recorded after equilibrium and were plotted against the milliequivalents of the OH^- ions added as shown in Fig. 1.

Thermal stability. Several 1-g portions of the exchanger were heated at various temperatures in a muffle furnace for 1 hr each. They were cooled to room temperature and their Na^+ IEC was determined as above by the column process. The results are shown in Table 3.

IR studies. The IR spectra of antimony(V) phosphate were taken by the potassium bromide disk method. Figure 2 shows the IR spectra of the material dried at room temperature and of the samples heated at various temperatures for 1 hr each to illustrate a gradual change in their peak intensities.

TABLE 3

EFFECT OF TEMPERATURE ON ION EXCHANGE CAPACITY OF ANTIMONY(V) PHOSPHATE ON HEATING FOR AN HOUR

Sample no.	Temperature (°C)	Na^+-ion exchange capacity (meq/dry g)	% Retention	Appearance
1.	45	1.75	100	Colorless
2.	100	1.75	100	Dirty white
3.	200	2.09	123	Dirty white
4.	400	0.60	35.3	Brownish
5.	600	0.315	18.5	Pale yellow
6.	800	0.09	5.5	Light yellow

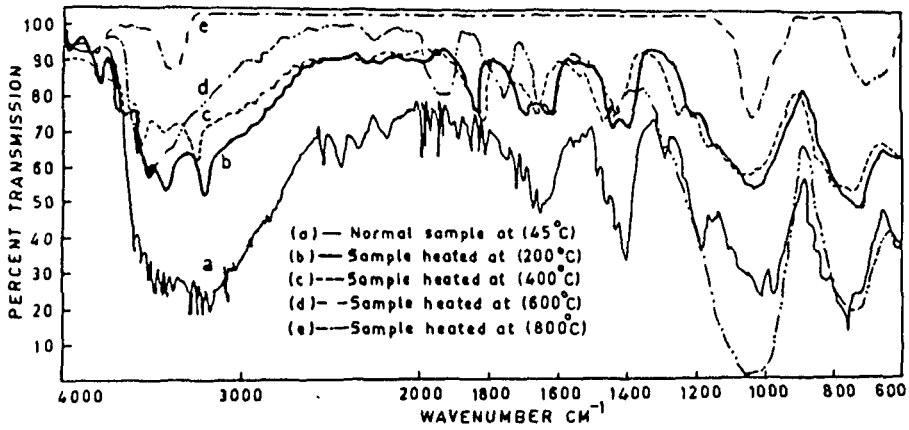


FIG. 2. Infrared spectra of normal and heated samples of antimony(V) phosphate cation exchanger.

Thermogravimetric studies. The thermogravimetry (TGA) curves are shown in Fig. 3 for the samples dried at 45 and 200°C. The differential thermal analysis (DTA) and derivative thermogravimetry (DTG) curves of the same samples are shown in Fig. 4.

Distribution studies. Distribution studies were performed for different metal ions in the various solvents as follows.

The exchanger beads (250 mg) in H^+ form were equilibrated with the selected solvents (25 ml) by shaking for approximately 4 hr in an electric shaker. The initial metal ion concentration was adjusted so that it may not exceed 3% of the total IEC of the material. The alkaline earth and transition metal ions were determined initially and after equilibration by the EDTA method (Reilley *et al.*, 1959). The alkali metals

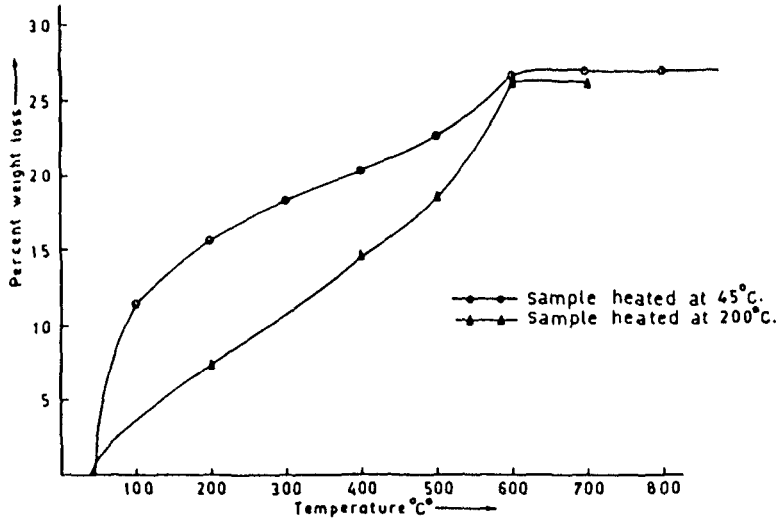


FIG 3 Weight loss as a function of heating temperature for antimony(V) phosphate heated at 45 and 200°C

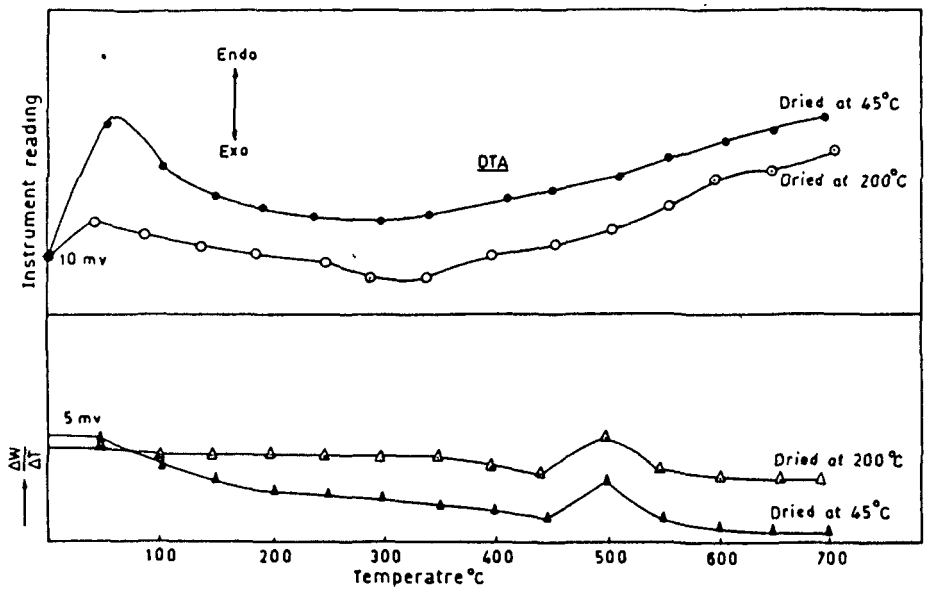


FIG. 4. Derivative and differential thermograms for the decomposition of antimony(V) phosphate.

were determined by flame photometry. The distribution coefficients were determined by the formula

$$K_D = \frac{I - F}{F} \times \frac{V}{A} \quad (\text{ml/g}),$$

where I is the initial amount of the metal ion in the solution phase, F is the final amount of the metal ion in the solution phase, V is the volume of the solution (ml), and A is the amount of the exchanger (g).

The results are summarized in Table 4.

Separations achieved. The 60- to 100-mesh-sized particles of the exchanger (2 g) in H^+ form were used for the column operation. The column was made in a glass tube of approx 0.6 cm i.d. The column was washed thoroughly with DMW and the mixture to be separated was loaded on it, maintaining a flow rate of approximately two to three drops/min. The separation was achieved by passing a suitable solvent through the column as eluant and the metal ions in the effluent were determined by the EDTA titrations as usual. Tables 5 and 6 summarize the salient features of the separations of Cd(II) and Hg(II) from some metal ions.

RESULTS AND DISCUSSION

Antimony(V) phosphate prepared in these studies has a superior cation exchange capacity when compared with the other materials of this class as indicated in Fig. 5. The ion exchange behavior of the material is highly reproducible and the material has good thermal and chemical stability (Fig. 6, Tables 2 and 3). The percentage retention in the ion exchange capacity of this material is about 35 even after heating up to 400°C. Further, there is an increase (approximately 20%) in its ion exchange

TABLE 4

K_D VALUES OF SOME COMMON METAL IONS ON ANTIMONY(V) PHOSPHATE IN VARIOUS MEDIA

Metal ion	K_D values				
	DMW	0.01 *M* HNO_3	0.1 *M* HNO_3	0.01 *M* $HClO_4$	0.1 *M* $HClO_4$
Mg(II)	388	63.7	59.0	147	19.5
Ca(II)	207	142	94.0	69.2	40.6
Sr(II)	243	136	53.3	155	40.0
Ba(II)	400	110	98.0	50.5	40.0
Cd(II)	18600	3640	648	675	120
Pb(II)	1950	626	161	176	21.0
Fe(III)	1106	278	85.0	34.0	45.0
Cu(II)	318	246	121	144	45.0
Ni(II)	370	66.0	28.0	24.9	15.4
Zn(II)	1840	428	394	316	42.5
Mn(II)	762	376	50.3	247	67.2
Hg(II)	12400	2846	456	355	90.0
Al(III)	56.2	40.7	26.0	52.0	26.0
Na(I)	250	60.0	16.6	25.0	12.5
K(I)	3200	1600	700	750	143
Cs(I)	900	450	233	600	400

capacity when dried at 200°C which is more than any other material as shown in Fig. 6.

The column elution experiments indicate a dependence of the eluant concentration on the rate of elution, which is a common phenomenon of such materials. The minimum molar concentration of a $NaNO_3$ solution used as an eluant is 1 *M* for the

TABLE 5

SOME SALIENT FEATURES OF SEPARATION OF Cd(II) FROM OTHER METAL IONS ON ANTIMONY(V) PHOSPHATE

Sample no.	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used	Eluant volume (ml)
1.	Mg(II)–Cd(II)	121.4 (Mg)	109.3	−9.96	1 *M* $HClO_4$	80
		533.8 (Cd)	545.1	+2.10	2 *M* HCl + 1 *M* HCl	80
2.	Ca(II)–Cd(II)	220.0 (Ca)	234.0	+6.36	1 *M* $HClO_4$	100
		533.8 (Cd)	545.0	+2.09	2 *M* HCl + 1 *M* KCl	100
3	Ba(II)–Cd(II)	549.0 (Ba)	549.0	0	1 *M* $HClO_4$	100
		533.8 (Cd)	550.0	+3.03	2 *M* HCl + 1 *M* KCl	100
4.	Ni(II)–Cd(II)	278.0 (Ni)	246.0	−11.51	1 *M* $HClO_4$	60
		533.8 (Cd)	511.0	−4.27	2 *M* HCl + 1 *M* KCl	100
5.	Cu(II)–Cd(II)	260.0 (Cu)	251.0	−3.46	1 *M* HClO	100
		533.8 (Cd)	539.0	+0.97	2 *M* HCl + 1 *M* KCl	100
6	Fe(III)–Cd(II)	251.0 (Fe)	212.0	−15.53	1 *M* $HClO_4$	120
		533.8 (Cd)	601.0	+12.55	2 *M* HCl + 1 *M* KCl	120

TABLE 6

SOME SALIENT FEATURES OF SEPARATION OF Hg(II) FROM OTHER METAL IONS ON ANTIMONY(V) PHOSPHATE

Sample no.	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used	Eluant volume (ml)
1.	Mg(II)–Hg(II)	121.4 (Mg)	122.6	+0.98	1 *M* $HClO_4$	100
		651.0 (Hg)	660.0	+1.68	2 *M* HCl + 1 *M* KCl	100
2.	Ca(II)–Hg(II)	204.0 (Ca)	202.0	−0.98	1 *M* $HClO_4$	140
		651.0 (Hg)	640.0	−1.68	2 *M* HCl + 1 *M* KCl	100
3.	Ba(II)–Hg(II)	549.0 (Ba)	596.0	+8.56	1 *M* $HClO_4$	140
		651.0 (Hg)	600.0	−7.83	2 *M* HCl + 1 *M* KCl	100
4.	Cu(II)–Hg(II)	254.0 (Cu)	274.0	+6.29	1 *M* $HClO_4$	100
		651.0 (Hg)	637.0	−2.15	2 *M* HCl + 1 *M* KCl	100
5.	Fe(III)–Hg(II)	251.0 (Fe)	241.0	−3.9	1 *M* $HClO_4$	120
		651.0 (Hg)	651.0	0	2 *M* HCl + 1 *M* KCl	120
6.	Ni(II)–Hg(II)	258.0 (Ni)	278.0	+7.99	1 *M* $HClO_4$	80
		651.0 (Hg)	651.0	0	2 *M* HCl + 1 *M* KCl	120

maximum elution of H^+ ions from a column of 1 g of the exchanger. The elution rate of the exchanger also appears to be quite fast as almost 95% of the H^+ ions are eluted out in the first 80 ml of the effluent from the column described above.

The pH titration curves obtained under the equilibrium conditions are shown in Fig. 1 for the LiOH/LiCl, NaOH/NaCl, and KOH/KCl systems. It is observed that a complete neutralization of the material is achieved by adding approximately 1.2 mmol of OH^- ions to the system containing 500 mg of the ion exchanger. The curves show another inflection at 1.8 mmol of the OH^- ions added, beyond which hydrolysis occurs. The exchange rates are in the order $Na^+ < K^+ < Li^+$ in the acidic range while a reversal occurs ($Li^+ < K^+ < Na^+$) in the basic pH range. However, the rate of the

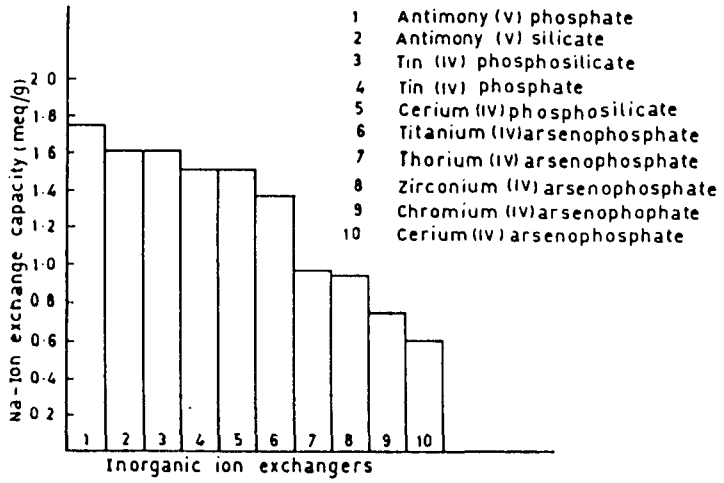


FIG. 5. Comparative statement of the ion exchange capacity of various ion exchangers.

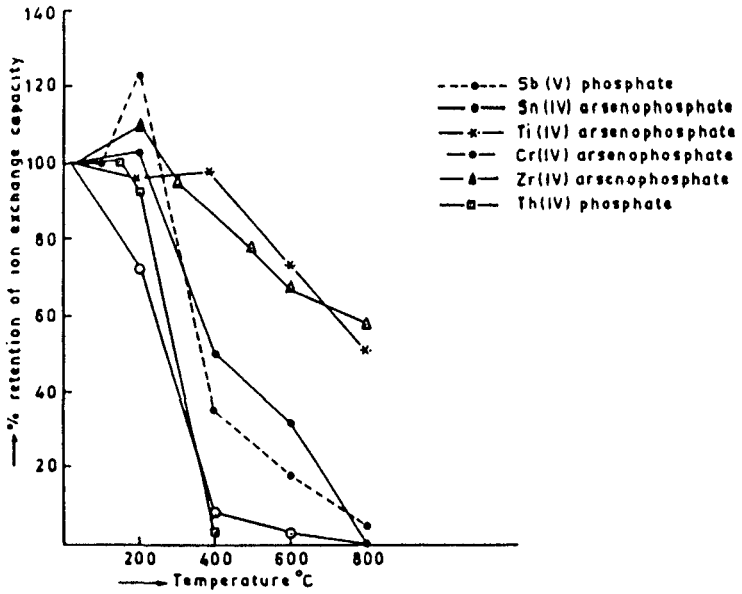


FIG. 6. Effect of heating on the IEC of various inorganic ion exchangers.

H^+–Li^+ exchange is slower than the H^+–Na^+ or H^+–K^+ exchanges throughout the whole pH range.

The IR spectra (Fig. 2) show the various peaks at around 750, 1050, 1200, 1400, 1600, and 3300 cm^{-1}. The peaks observed at 750 and 1050 are indicative of the metal–oxygen stretching vibrations while those at 1200 and 1400 are due to the presence of phosphate groups. The presence of water of crystallization is indicated by the peaks at 1600 and 3300 cm^{-1}. The peaks at 1600 cm^{-1} are also indicative of the strongly hydrogen-bonded OH or extremely strongly coordinated H_2O. On heating the exchanger at various temperatures the peak intensities are affected as shown in Fig. 2. A sample heated up to 800°C gives only three peaks, representing simply the antimony oxide and the water of crystallization (Rao, 1963).

Chemical analysis of the material gives the empirical formula

$$(Sb_2O_5)_2 \cdot (H_3PO_4)_3 \cdot nH_2O.$$

If it is assumed that the external water is lost at 200°C (Fig. 3), then on the basis of the thermogravimetric studies we have the following relation between n, the number of external water molecules per molecule of the material, and x, the percentage weight loss due to the removal of external water molecules,

$$\frac{1800n}{M + 18n} = x,$$

where M is the molecular weight of the exchanger excluding the external water molecules. It determines that n is 10.6. Since the X-ray studies point out its amorphous nature, further elucidation of its structure cannot be given at this stage.

Figure 4 gives the DTG and DTA curves showing the decomposition of antimony

phosphate. As is clear from the DTG curve the rate of change of weight is quite sharp at 500°C, indicating the weight loss due to the condensation process as follows:

$$(Sb_2O_5)_2 \cdot (H_3PO_4)_3 \rightleftharpoons 2Sb_2O_5 + \tfrac{3}{2}P_2O_5 + \tfrac{9}{2}H_2O.$$

This process accounts for a further loss of 4.5 H_2O molecules from a molecule of the exchanger giving rise to a total weight loss at this temperature of approximately 23% as shown by the thermogram (Fig. 3). The DTA curve shows an endothermic peak near 100°C as the sample requires energy to break bonds in the elimination of the external water molecules.

The column experiments in the laboratory have illustrated well the separations of Cd(II) and Hg(II) from other metal ions such as Cu(II), Fe(III), Ni(II), Mg(II), Ba(II), and Ca(II) which were tried on the basis of the distribution studies (Table 4). Tables 5 and 6 summarize the essential features of these binary separations. Synthetic mixtures containing Cd(II) and Hg(II) with an excess of the other metal ions mentioned above were also prepared to take into account situations in which polluted water may contain these metals in much higher concentrations. In all cases the results obtained were within the same error range as indicated in the tables.

CONCLUSION

Antimony(V) phosphate, prepared in these studies as a new inorganic ion exchange material, demonstrates a considerably higher affinity for Cd and Hg than other metals. It therefore appears to be of great promise in the field of pollution science where an effective separation method of these metals from other pollutants is needed.

ACKNOWLEDGMENTS

The authors thank Professor K. T. Nasim for research facilities and the Council of Scientific and Industrial Research (India) for financial assistance.

REFERENCES

ABE, M., AND ITO, T. (1968) *Bull Chem Soc Japan* **41**, 333.

BAETSLE, L. H., AND HUYS, D. (1969) *Belg Patent* **649**, 746.

BELINSKAYA, F. A., MIRITSINA, E. A., AND RUNEVA, T. N. (1976). *Izv Akad Nauk SSSR Neorg Mater* **12**, 1631

NOVIKOV, B. G., BELINSKAYA, F. A., AND MATEROVA, E. A. (1976). *Fiz Khim* **1**, 94

VARSHNEY, K. G., SHARMA, U., RANI, S., AND PREMADAS, A. (1982–1983). *Sep Sci Technol* **17**, 1527.

VARSHNEY, K. G., AND RANI, S. (1983) *Indian J Chem A* **22**, 657

VARSHNEY, K. G., RANI, S., AND SINGH, R. P. (1985). *Ecotoxicol Environ Safety* **10**, 309.

SANDELL, E. B. (1959) *Colorimetric Determination of Traces of Metals*, Vol. III, p. 266. Interscience, New York

OLSEN, S. R., COLE, C. V., WATANABE, F. S., AND DEAN, L. A. (1954). *U.S. Dep. Agric. Circ* **939**, 99

TOPP, N. L., AND PEPPER, K. W. (1949) *J Chem Soc* 3299.

REILLEY, C. N., SCHMIDT, R. W., AND FAWZYS (1959). *J Chem Ed* **36**, 555.

RAO, C. N. R. (1963) *Chemical Applications of Infra-red Spectroscopy* Academic Press, New York.

IJEP 9 (8) : 574 - 576

2.5 Adsorption Behaviour of Antimony(V) Phosphate for α - Amino Acids : Some Binary Separations onits Column

K. G. Varshney, A. A. Khan and S. M. Maheshwari

Aligarh Muslim University, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh - 202 002

Column chromatographic separation of amino acids on molecular sieves and organic resins are well known. However, inorganic ion exchangers are not so common for such applications, although they have shown promising ion exchange behaviour and stability when compared with organic resins. The present study explores the possibility of using an inorganic material, antimony(V) phosphate as a new cation exchanger for the quantitative binary separations of some α -amino acids. The methods of preparation of the material and distribution behaviour for amino acids have been studided. As a result a suitable material has been developed for the binary separation of some α - amino acids.

INTRODUCTION

Column chromatographic separation of amino acids on molecular sieves (Moore and Stein, 1948) and organic resins (Bonman and Eichorn, 1947; Moore and Stein, 1949) is quite common. However, the use of inorganic ion exchangers for such a study is not well known although these materials are well established and have shown some quite interesting applications. The present work is, therefore, aimed to explore the possibility of using inorganic ion exchangers for the adsorption of amino acids. The amino acids selected are of general occurrance in human beings and plants, Antimony(V) phosphate has been taken as the adsorbent because of its excellent ion exchange properties and separation potential already studied earlier in these laboratories (Varshney and Maheshwari).

EXPERIMENTAL

Reagents and chemicals

Antimony(V) chloride used in this study was of 98 % purity obtained from FLUKA (Switzerland) and the tri - sodium ortho - phosphate was a B.D.H. Pool (England) product. All other reagents and chemicals were of Analar grade.

Apparatus

A Bausch and Lomb spectronic - 20 spectrophotometer was used for colorimetric studies. For the equilibrium studies a water - bath incubator shaker having a temperature variation of ±2 °C was used. The pH measurements were performed on an ELICO (India) model L1 - 1OT pH - meter.

Preparation of reagent solutions

A stock solution (1.58M) of antimony(V) chloride ($SbCl_5$) was prepared in 4M HCl. Further dilutions were also made in 4M HCl. Tri - sodium orthophosphate ($Na_3PO_4 . 12 H_2O$) was dissolved directly in demineralized water (DMW) to prepare its solution of a desired concentration.

Synthesis of antimony(V) phosphate

Antimony(V) phosphate was synthesized by the standard method reported earlier(Varshney and Maheshwari). Antimony(V) chloride (0.1M) and tri - sodium orthophosphate (0.05M) solutions were mixed in a volume ratio 1 : 1. The pH of the solution was adjusted between 0 - 1. The gel thus obtained was kept for 24 hr at room temperature (app. 30 °C) and filtered by suction. The excess acid was removed by washing with DMW and the gel was dried in an air oven at 45 °C. The dried material was converted into small granules by putting in DMW and converted into the H^+ - form by treating with app. 1M HNO_3 for 24 hr shaking occasionally and replacing intermittantly the supernatant liquid. The material thus obtained was finally washed to a pH 6 - 7 and dried at 45 °C as above. The ion exchange capacity was determined by the usual column process and was found to be 1.75 meq/gm.

Preparation of different buffer solutions used as solvent systems

Buffer solutions of varying pH were obtained by mixing the following amounts (ml) of a 0.2M NaOH solution with a 100 ml mixture consisting of the 0.004 moles each of the phosphoric, acetic and boric acids (Ju Lurie, 1975). The numbers in the parantheses indicate the resulting pH of the mixture : 35.0 (2.20), 45.0 (3.30), 50.0 (4.1), 60.0 (5.2), 67.0 (5.95), 72.5 (6.6) and 80.0 (7.25).

Determination of α - amino acids

α - amino acids were determined by the standard ninhydrin method reported by Moore and Stein (1948). First a ninhydrin reagent solution was prepared by *mixing the solutions* (500 ml each) of hydrated stannous chloride (800 mg in 500 ml citrate buffer of pH 5.0) and ninhydrin (20 gm in 500 ml of methyl cellosolve). Citrate buffer was prepared by dissolving 21 gm of citric acid in 200 ml of 1M NaOH and making the volume 500 ml with glass distilled water.

Distribution studies

200 mg of the exchanger in H^+ form were shaken in an electric shaker at 30 ± 2 °C for 4 hr with 1 ml of 0.1 % α - amino acids and 19 ml of different solvent systems (buffer solutions of various pH values). The amounts of α - amino acids in different solvent systems before and after the equilibrium were determined spectrophotometrically by ninhydrin method as discussed above. The distribution coefficient (Kd) for different α - amino acids in variousbuffered solutions are given in table 1. The following formula was used for the calculation of Kd values :

$$Kd = \frac{I - F}{F} \times \frac{V}{M} \text{ ml/gm}$$

where, I is initial concentration of amino acids. F is final concentration of amino acids, V is total volume of the solution (ml), and M is mass of the exchanger (g).

Separations achieved

Table 2 shows the binary separations achieved using glass column (i.d. 1 cm) containing 2 gm exchanger with all the details, such as amount of the α - amino acid loaded and recovered along with the % error in each case.

Table 1. *Kd values of some common α -amino acids on antimony(V) phosphate in buffers of different pH*

Amino acid	pH						
	2.20	3.30	4.10	5.20	5.95	6.60	7.25
Glycine	26.10	10.50	5.80	0.00	11.80	17.60	14.60
L-Leucine	5.00	15.00	29.10	29.10	29.10	45.80	21.05
DL-Serine	333.33	62.50	30.00	0.00	0.00	0.00	30.00
L-Cystine	60.00	56.35	200.00	160.00	14.15	6.25	6.25
DL-Valine	700.00	166.67	10.00	13.04	4.54	0.00	11.10
Glutamic acid	325.00	121.00	10.00	33.33	35.50	18.00	16.00
L-Histidine	29.63	30.00	21.67	7.14	8.69	130.00	91.42
L-Lysine-HCl	3.45	8.04	21.05	31.34	32.83	23.29	24.66
DL-Alanine	27.47	38.09	30·77	38.71	35.00	50.91	52.73
L-Tyrosine	25.00	7.00	50.00	141.00	15.00	10.00	7 00
DL-Tryptophan	25.00	94.00	29.60	45.00	34.60	16.60	94.40
DL-Aspartic acid	300.00	242.80	106.90	100.00	700.00	60.00	20.00
DL-2-Amino n-n butyric acid	190.90	120.60	137.00	16.50	57.10	6.60	6.90
DL-Nor leucine	177.70	56.20	25.00	25.00	28.20	38.40	6.90
DL-L-Cystiene	162.50	40.00	40.00	50.00	23.50	16.60	10.50
DL-iso Leucine	247.80	185.70	150.00	11.10	77.70	77.70	66.60
DL-Threonine	166.60	158.00	100.00	8.10	60.00	12.90	175.80
DL-B Phenyl alinine	780.00	476.90	188.40	29.30	78.50	134.30	177.70
L-Arginine mono HCl	500.00	215.00	130.70	100.00	9.10	25.00	33.30
DL-Methionine	766.00	466.60	81.30	85.70	54.70	20.00	188.80

Table 2. *Some quantitative binary separations of α-amino acids on antimony(V) phosphate column*

Amino acid	pH	Amount loaded, mg	Amount found, mg	Percent error
Glycine-	2.5	10.00	10.50	+5.0
DL-Valine	4.1	5.40	5.88	+8.8
Glycine-	2.5	10.00	10.92	+10.4
L-Glutamic acid	5.2	8.00	7.70	-3.7
L-Leucine-	2.5	19.20	21.00	+9.4
DL-Valine	4.1	5.40	5.76	+6.5
L-Leucine-	2.5	11.80	12.48	+5.7
L-Glutamic acid	5.2	8.00	8.74	+9.25
DL-Serine-	2.2	8.80	9.46	+7.5
DL-Valine	4.1	5.40	5.94	+10.1
SL-Serine-	2.2	8.80	10.08	+13.3
L-Glutamic acid	5.2	8.00	8.68	+8.5

RESULT AND DISCUSSION

The main feature of these studies has been to develope a simple and precise method for some binary separations of α - amino acids. Table 1 summarizes the distribution coefficients of 20 amino acids in various pH media on antimony(V) phosphate. It was observed that the control of pH is especially important for the adsorption as well as for the separation of α - amino acids on the surface of antimony(V) phosphate. As the results indicate the adsorption is, in general, greater at lower pH values for almost all amino acids except L - histidine and L - lysine. In acidic media the amino acids are protonated to form cations and should have a greater affinity towards a cation exchanger. L - histidine and L - lysine with excess amino groups may have an attraction of protons present in the ion exchanger matrix at nearly neutrol pH. Table 2 shows the dntails of some binary separations of -amino acids achieved on the antimony(V) phosphate columns based on the Kd values. It is clear from this table the separations of both natures, that is neutral from neutral and neutral from acidic amino acids have been possible by this method.

ACKNOWLEDGEMENT

The authors thank Prof. K.T. Nasim for the research facilities and the Council of Scientific and Industrial Research for the financial assistance.

REFERENCE

Bonman, W.C. and J.E. Eichorn. 1947. *J. Am. Chem. Soc.*, 69 : 2830.

Ju Lurie. 1975. Handbook of analytical chemistry. Mir Publishers. pp 263.

Moore, S. and W.H. Stein. 1948. *J. Biol. Chem.*, 176 : 367.

Moore, S. and W.H. Stein. 1949. *J. Biol. Chem.*, 178 : 53.

Varshney, K.G. and S.M. Maheshwari. *J. Ecotox. Env. Safety*. In Press.

SEPARATION SCIENCE AND TECHNOLOGY, 17(13 & 14), pp 1527–1543, 1982-83

2.6 Cation-Exchange Study on a Crystalline and Thermally Stable Phase of Antimony Silicate. Effect of Irradiation on Ion-Exchange Behavior and Separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II), Ca(II), and Sr(II)

K G. VARSHNEY, UMA SHARMA, SIMA RANI, and A PREMADAS

CHEMISTRY SECTION
Z H COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH 202001 INDIA

Abstract

A systematic ion-exchange study has been performed on antimony silicate, which includes its ion exchange capacity, elution behavior, pH titrations, and distribution coefficients of common metal ions The K_d values for alkali metals vary with the pH of the solution and the material is found to be highly selective for Rb(I) at pH values greater than 1 On the basis of distribution studies, the separation of Cd(II) from Zn(II) and Mn(II) has been achieved Similarly, Mg(II) has been separated from Ba(II), Ca(II), and Sr(II) to illustrate its utility Antimony silicate is very stable both thermally and chemically and possesses reproducible ion-exchange properties, also, the effect of irradiation on the ion-exchange behavior is negligible A tentative formula of the material has also been proposed based on chemical, infrared, and thermogravimetric analysis studies The x-ray studies reveal that the exchanger is crystalline with a d-value of 6 09 Å

INTRODUCTION

Silicates form one of the most important classes of the ion-exchange materials as they are temperature resistant and stable under chemical attack (*1–4*). Antimony salts such as Zr(IV), Ti(IV), and Sn(IV) antimonates (*5–8*) have received attention because of their reproducible ion-exchange behavior while the antimony-silicon cation exchangers have been prepared and

studied by Novikov and co-workers (*9–13*). However, a systematic ion-exchange study of antimony silicate has been lacking. Our study is summarized in the following pages. The effect of irradiation on the ion-exchange properties of this material is also included.

EXPERIMENTAL

Reagents

The antimony pentachloride used in this study was of ~95% purity obtained from Koch-Light Laboratories Ltd. (Colnbrook, Bucks, England) and the sodium silicate was a Riedal (DEHAENAG, Seelze-Hannover) product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH measurements were made on an Elico (India) model LI-10 pH meter while infrared studies were performed on a Beckmann IR-20 spectrophotometer. X-ray studies were made on a Philips X-ray unit using a Mo-K_α target, and the radioactivity was measured in a well-type single channel counter of the Electronics Corporation of India Ltd. using a NaI(Tl) detector. A Bausch and Lomb spectronic-20 colorimeter was used for the spectrophotometric studies.

Preparation of the Reagent Solutions

A stock solution (1.0 *M*) of antimony pentachloride was prepared in concentrated HCl and was diluted to the desired concentration with demineralized water (DMW) so that the final concentration of HCl was not less than 4 *M* in the solution. Sodium silicate was dissolved directly in DMW by heating. For distribution studies, the metal salts were also generally dissolved in DMW except the tri- and tetravalent metals for which 2–3 drops of the corresponding acids were necessary to prevent hydrolysis.

Synthesis of the Material

Different samples of antimony silicate were prepared by varying the concentration of the mixing solutions as given in Table 1 and the pH was fixed in the range 0–1 by adding HNO_3 with constant stirring. The gel thus obtained was kept at room temperature (30°C) overnight, filtered, washed

TABLE I
Preparation of Antimony Silicate (SbSi)

Sample	Concentration of each mixing solution (*M*) ($SbCl_5$ + Na-silicate)	Mixing ratio (Sb:Si) by volume	Ion exchange capacity (meq/g)
S-1	0.5	1:1	Unstable in solution
S-2	0.4	1:1	1.6
S-3	0.3	1:1	1.7
S-4	0.2	1:1	1.5
S-5	0.1	1:1	1.7
S-6	0.1	1:2	1.6

with DMW, and dried at 45°C in an air oven. It was then immersed in DMW and the granules were converted into the H^+ form as usual (*14*). On the basis of its apparent chemical stability and general appearance, Sample S-6 was selected for further study. The reproducibility was checked by preparing the samples several times by the same procedure.

Composition

250 mg of the powdered exchanger was fused with ~4 g of Na_2CO_3 in a platinum crucible and transferred in a 100-mL solution of 4 *M* HCl. The amounts of antimony and silica in this solution were determined by standard methods (*15, 16*) and were found to be in the mole ratio 1:3.

Chemical Stability

250 mg of the material was placed in a 25 mL solution of an acid or a base with intermittant shaking for 24 h. The solution was then analyzed for the dissolved antimony and silica content using standard spectrophotometric methods (*17, 18*). The results are shown in Table 2.

Irradiation Studies

Antimony silicate (S-6) was irradiated by γ-rays obtained from a ^{60}CO source for 96 h under a dose rate of 0.4 Mrd/h using $FeSO_4$ as the dosimatter.

TABLE 2
Chemical Stability of SbSi

Solvent	Amount dissolved in (mg) per 25 ml	
	Sb	Si
1 *M* HNO_3	0 65	0 00
2 *M* HNO_3	2 34	0 00
4 *M* HNO_3	2 95	0 07
1 *M* HCl	1 31	0 00
2 *M* HCl	1 40	0 00
4 *M* HCl	5 51	0 00
1 *M* H_2SO_4	1 68	0 00
4 *M* H_2SO_4	3 50	0 00
2 *M* $NaNO_3$	0 00	2 02
4 *M* $NaNO_3$	0 23	2 02
2 *M* KNO_3	0 09	1 55
0 05 *M* NaOH	4 58	3 50
0 1 *M* NaOH	Dissolved appreciably	Dissolved appreciably
0 1 *M* KOH	Dissolved appreciably	Dissolved appreciably
0 1 *M* NH_4OH	1 68	3 15
0 5 *M* NH_4OH	4 44	3 15

Ion-Exchange Capacity (i.e.c.)

The i.e.c. was determined as usual by the column process taking 1 g exchanger (H^+-form) in a glass tube of i.d. ~1 cm and maintaining the flow rate at ~0.5 mL/min. The total volume of the eluant necessary for the complete elution of H^+-ions was 250 mL and the values in meq/dry g for different metals were Li(I) 1.05, Na(I) 1.60, K(I) 1.49, Mg(II) 1 53, Sr(II) 1.59, Ca(II) 1.10, Ba(II) 1.61, NH_4(I) 0.8.

Thermal stability

Several 1.0-g portions of Sample S-6 were heated at various temperatures in a muffle furnace for 1 h each, and the i.e.c. was determined as above by the column process after cooling them to the room temperature. The i e c. was also determined after heating the sample for 4h at 400 and 800°C

Elution Behavior

Since the extent of elution depends upon the concentration of the eluant, a fixed volume (125 mL) of $NaNO_3$ solution of varying concentrations was passed through a column containing 0.5 g of the exchanger. It was observed that a 1.0 *M* concentration is sufficient for the complete elution of H^+-ions from this column. The elution was therefore done with a 1.0 *M* solution of $NaNo_3$ as an eluant. Figure 1 shows the histograms of the γ-irradiated and unirradiated samples of Sb(V) silicate.

pH Titrations

These were performed by the Topp and Pepper's method (*19*) by placing 500 mg of the exchanger in several 250 mL conical flasks, followed by equimolar solutions of alkali metal chlorides in different volume ratios, the final volume being 50 mL. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of the OH added. The experiment was repeated for the irradiated sample and the results are summarized in Fig. 2.

Distribution Studies

For Some Common Metal Ions

250 mg of the exchanger in the H^+ form were shaken at 30 ± 2°C for 4 h with a 25-mL solution containing the metal ion. The initial and final concentrations of the metal ion in the solution were determined by EDTA titrations (*20*) as usual (*21*). The K_d values obtained are summarized in Table 3.

For Alkali Metals

The K_d values for Na(I), K(I), Rb(I), and Cs(I) were determined using radiotracers. For this purpose 100 mg of the material in the H^+ form equilibrated with 20-mL of the solvent containing 1.0 mL of the tracer and 1.0 mL of the carrier solution of the required concentration. The initial and final metal concentrations in solution were determined by measuring the activity of the solution in the two cases. The K_d values were calculated with the following formula:

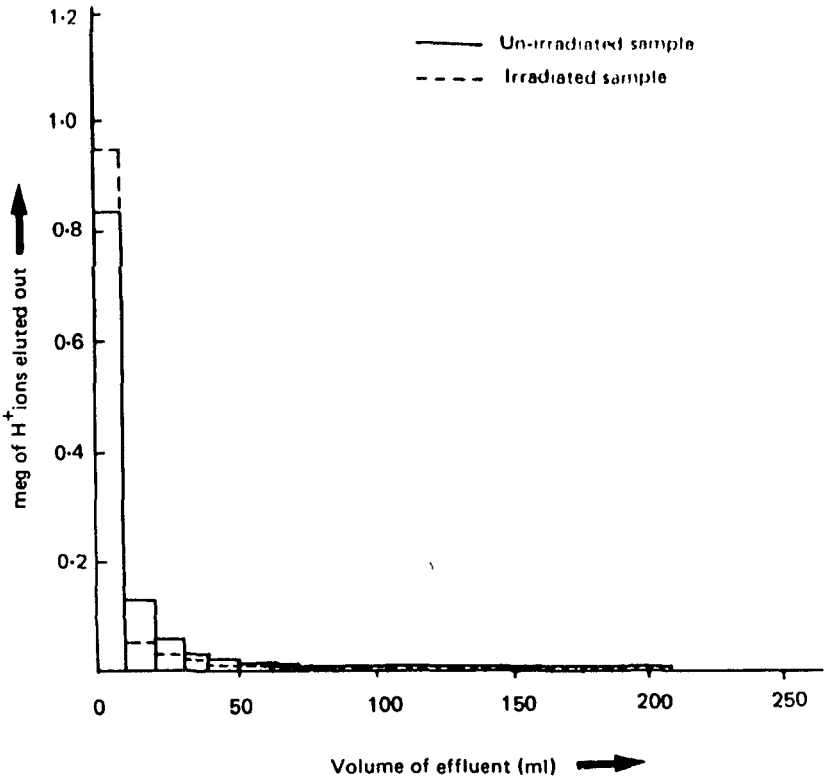


FIG. 1. Histograms showing the elution behavior of antimony(V) silicate exchanger

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ mL/g}$$

where I = initial volume of the EDTA used or initial activity of the solution
F = final volume of the EDTA used or the final activity of the solution
V = volume of the solution
M = mass of the exchanger

The following radiotracers were used in these studies with their half-life periods shown in parentheses: ^{24}Na (15 h), ^{42}K (12.5 h), ^{86}Rb (18.7 d), ^{137}Cs (30.2 years), ^{54}Mn (31.3 d), and ^{203}Hg (46.6 d). Figure 3 shows the variation of K_d values with the pH for different alkali metals.

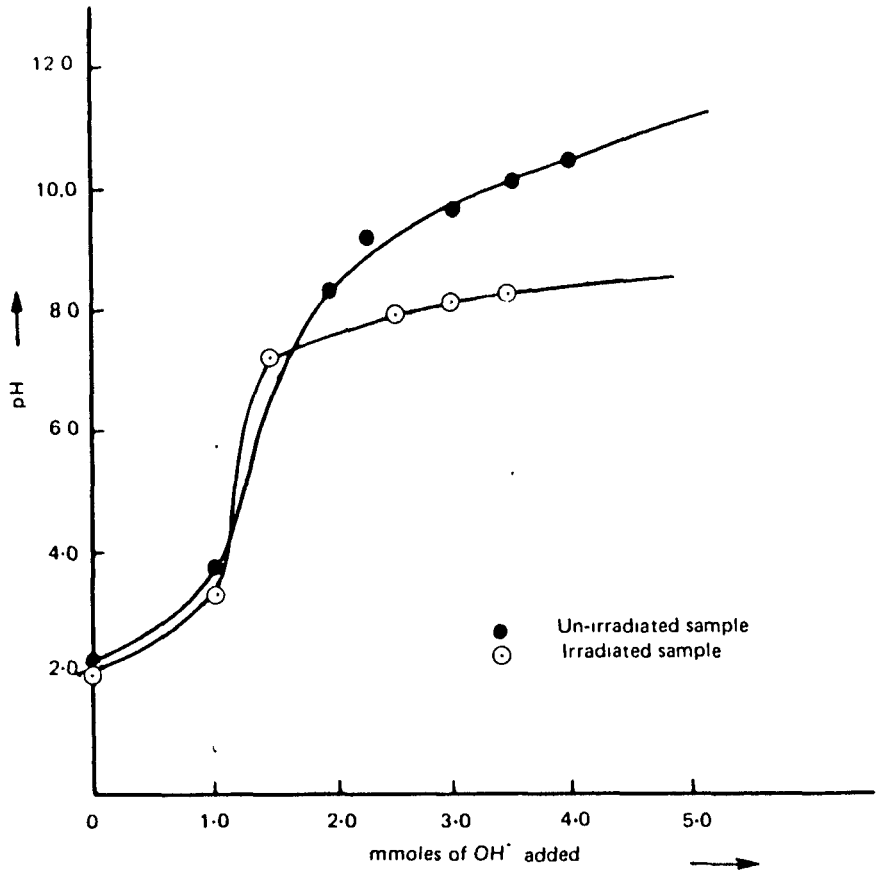


FIG 2 pH titration curves for antimony(V) silicate

Separations Achieved

Several binary separations were tried using a column containing 2 g of the sized (50-100 mesh) exchanger particles taken in a glass tube having an i.d. of ~0.6 cm. The flow rate was fixed as ~0.5 mL/min using eluants selected on the basis of the K_d values obtained.

RESULTS AND DISCUSSION

These studies reveal that antimony silicate is a highly stable and reproducible ion-exchange material. A comparison of its thermal stability

TABLE 3
K_d Values of Some Common Metal Ions on Antimony-Silicate in Different Media[a]

Metal ion	Solvent: pH:	DMW 7	0.01 *M* $HClO_4$ 2	0.01 *M* $HClO_4$ 1	10% HCl + 25% DMSO (1:20) 1.6	10% HCl + 25% DMSO (1:10) 1.2	10% HCl + 25% DMSO (1:5) 0.9	10% HCl + 25% DMSO (1:1) 0.4
				K_d values				
Zn(II)		TA	1800	36	159	39	19	0
Cd(II)		TA	1900	1900	900	900	900	900
Hg(II)		TA	TA	1250	0	0	0	0
Mn(II)		TA	433	14	28	10	0	0
Mg(II)		TA	357	12	33	14	0	0
Ca(II)		TA	TA	TA	1500	1500	1500	357
Sr(II)		TA	TA	TA	TA	1350	1350	480
Ba(II)		TA	TA	1153	1153	616	526	150
Cu(II)		TA	TA	255	220	52	18	0
Ni(II)		TA	900	620	36	20	7	0
VO(II)		TA	866	16	45	32	16	0
Pb(II)		TA	TA	1400	TA	1400	1400	328
Co(II)		TA	655	54	78	54	36	13
Fe(III)		TA	TA	175	633	214	0	0
Al(III)		TA	TA	37	149	44	0	0
Zr(IV)		TA	TA	TA	800	1250	1250	1250
Th(IV)		TA	TA	600	1066	60	218	62
Y(III)		TA	TA	424	TA	424	1203	92
La(III)		TA	TA	572	TA	1000	450	312

[a]TA = total adsorption.

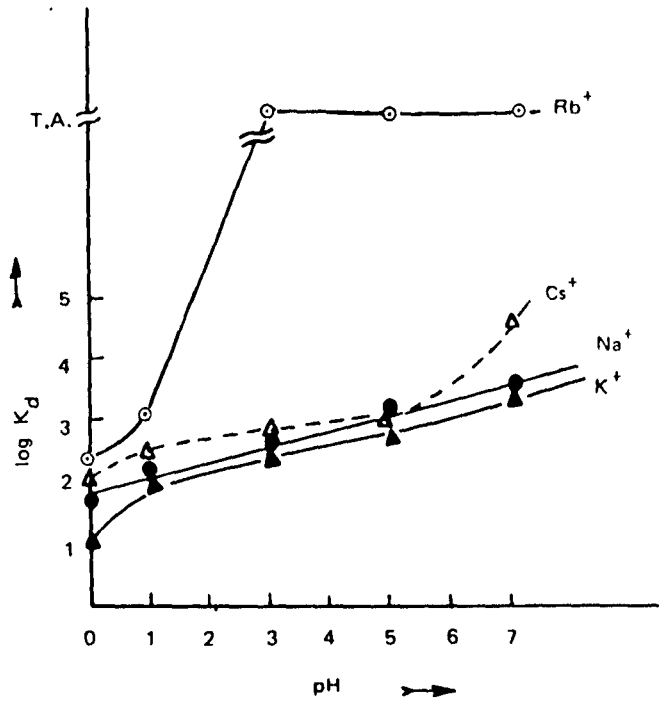


FIG. 3. Effect of pH on the K_d values of alkali metals on antimony(V) silicate

with other exchangers of this class (Fig. 4) indicates a high percent retention in its i.e.c. on heating, almost comparable with the zirconium(IV) and titanium(IV) arsenophosphates prepared earlier (*21*). At 400 C, even heating for 4 h does not alter its i.e.c. appreciably, as seen in Table 4. This material also appears to be highly chemically stable (Table 2). The elution behavior indicates that the exchange is quite fast and almost all of the H^+-ions are eluted out in the first 50 mL of the effluent from a column of 1.0 g exchanger (Fig. 1). Moreover, the exchange takes place in one step as indicated by the pH titration curve shown in Fig. 2.

The distribution studies illustrate some of the interesting features of this material. A plot of pH versus log K_d for Na(I) and K(I) is a straight line; however, there is a positive deviation in this behavior for the Cs(I) ion above pH 5 (Fig. 3). For Rb(I), the material shows a total adsorption even above pH 1. In this respect, antimony silicate is different from Sn(IV) arsenophosphate (*22*) which shows a linear increase in K_d values for Rb(I) and Cs(I) with pH. Antimony silicate, therefore, appears to be specific for the Rb(I) ion and can be used for its extraction.

TABLE 4
Ion-Exchange Capacity and Appearance of SbSi After Heating to Various Temperatures

Drying temperature (°C)	Time of heating (h)	Na ion exchange capacity (meq/dry g)	Appearance
45	1	1 60	White
100	1	1 52	White
300	1	1 42	Yellowish white
400	1	1 25	Yellowish white
600	1	1 20	Dark yellow
800	1	0 72	Yellowish white
400	4	1 18	Yellowish white
800	4	0 34	Yellowish white

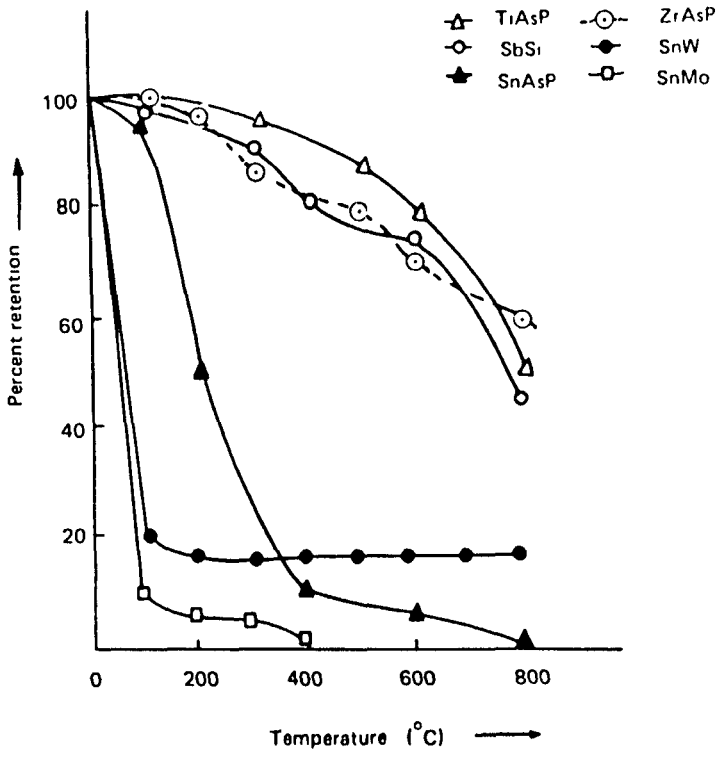


FIG 4 Percent retention of the H^+ ions in the exchanger phase on heating

On the basis of its chemical composition, pH titration, and TGA results, the antimony silicate, prepared in these studies, may be tentatively assigned the following formula: $[Sb_2O_5(H_2SiO_3)_6] \cdot nH_2O$

If it is assumed that all the exchangeable water molecules are removed on heating up to ~280°C, the first inflection point in the TGA curve (Fig. 5), the value of n can be calculated from

$$18n = \frac{X(M + 18n)}{100}$$

where X is the % weight loss (20%) in the exchanger on heating up to the inflection temperature and M is its molecular weight. The value of n thus obtained is 11. A further loss in weight above 280°C may be due to the

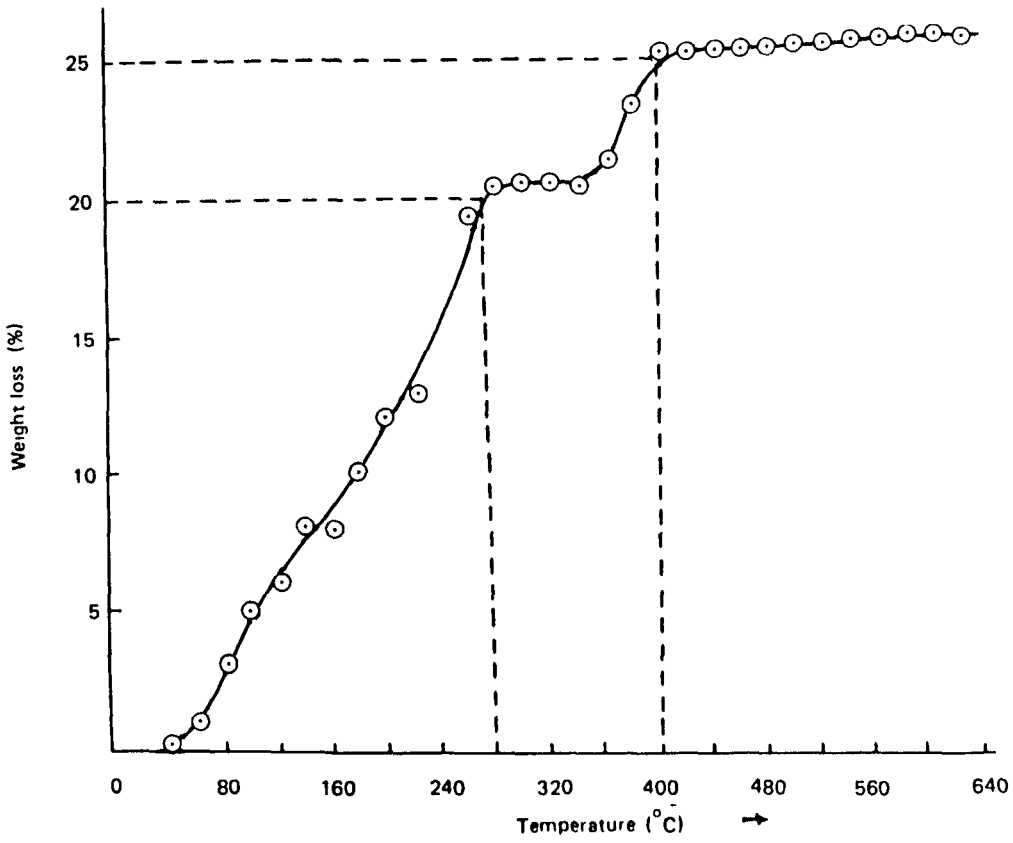


FIG. 5. Thermogram of antimony (V) silicate.

condensation process which probably continues up to 400°C, beyond which the oxides of Sb and Si are probably formed. An exhibition of the i.e.c. of SbSi even after heating to this temperature may be accounted for by the formation of antimonic acid when the oxide is dipped in aqueous solution. Antimonic acid has earlier been studied (*10, 23, 24*) as a cation exchanger.

The IR spectra show the peaks at ~450, 750, 1050, 1600, and 3300 cm^{-1} which represent (*25*) the presence of metal hydroxides (450 and 750) silicates (1050) and H_2O molecules (1600 and 3300) in the structure. The x-ray studies reveal the crystalline behavior of the material with a *d*-value 6.09 Å.

An irradiation of the sample by γ-rays for 96 h under a dose rate of 0.4 Mrd/h does not significantly change the ion-exchange behavior and the selectivity of metal ions as indicated in Table 5. Only a slight change in the elution rate (Fig. 1) and pH titration behavior (Fig. 2) is observed on irradiation.

The utility of this material was demonstrated by achieving separations of great analytical significance; for example, Mg(II) was separated from other alkaline earths (Figs. 6 and 7). Similarly, the rather difficult separation of Cd(II) from Zn(II) was performed on this ion-exchanger with a simple eluant 1 *M* $HClO_4$ (Fig. 8). Binary separations like Cd–Mn and Hg–Pb were achieved on the columns of SbSi. Although antimonic acid has earlier shown (*10*) a great affinity for Cd(II), it could not be utilized for its separation from Zn(II). For this purpose the SbSi exchanger prepared in these studies seems to have an added advantage. Table 6 shows the details of the six binary separations achieved on the column of this exchanger. It is clear from Table 6 that the % error observed in all cases is reasonably low and the separations can be said to be precise.

TABLE 5
Effect of Irradiation on the Adsorption of Mn^{2+}, Hg^{2+}, and Cs^+ on SbSi

	K_d values			
	Water		$HClO_4$	
Metal ion	Normal sample	Irradiated sample	Normal sample	Irradiated sample
Mn^{2+}	473	515	34.0	44.0
Hg^{2+}	420	373	102	194
Cs^+	38,394	36,298	97	110

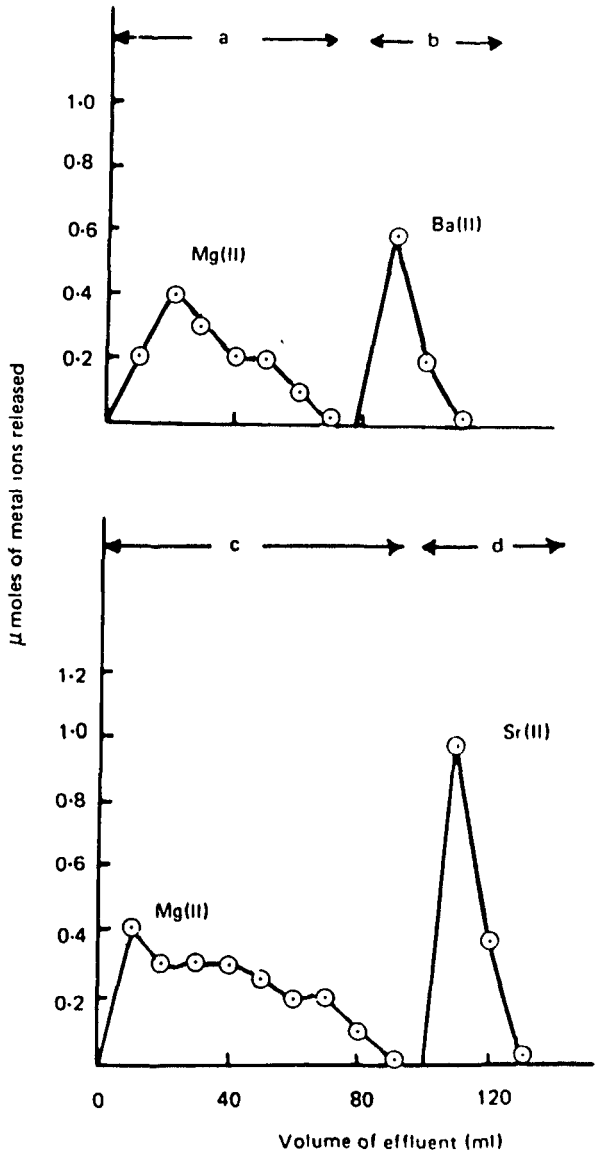


FIG. 6 Separationof Mg(II) from Ba(II) and Sr(II) on antimony(V) silicate columns (a) and (c), 0.1 *M* $HClO_4$; (b) and (d) 1 *M* $HClO_4$

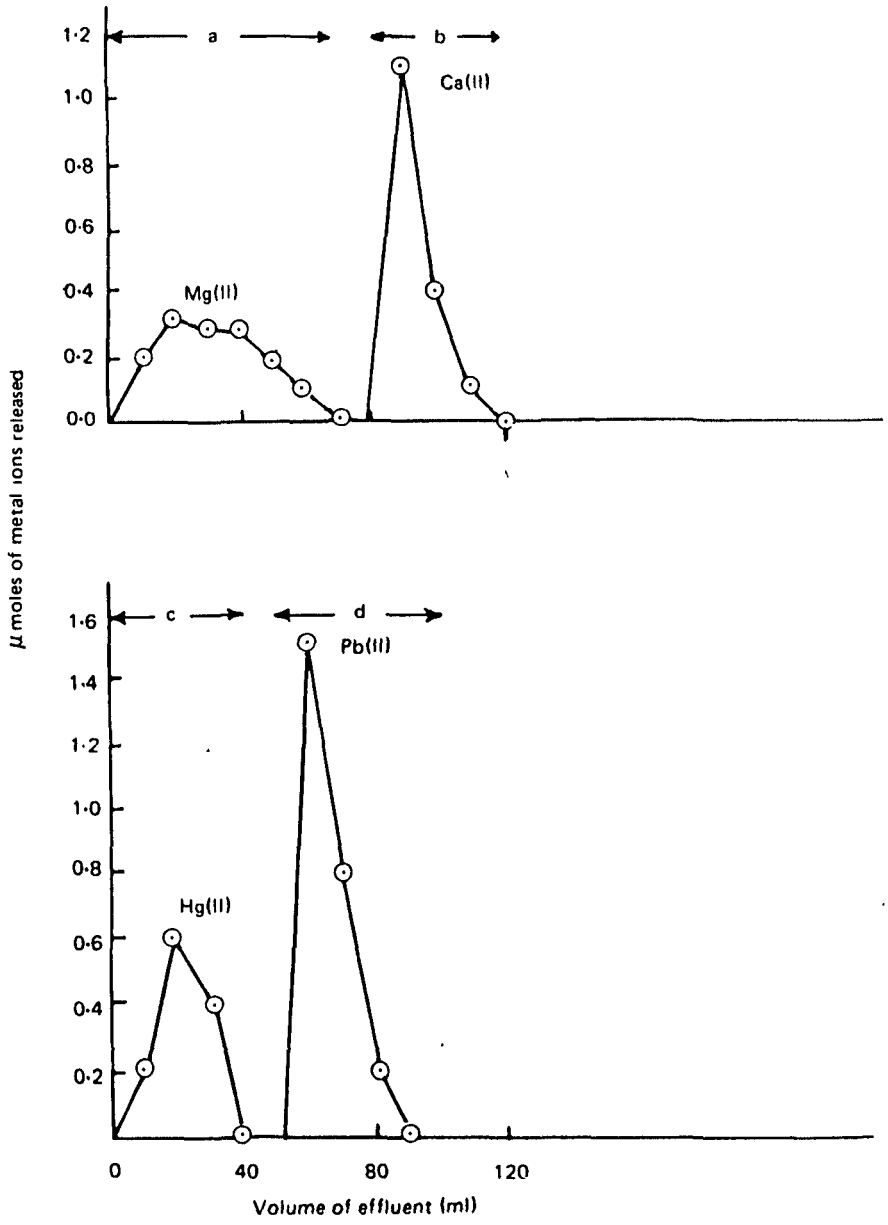


FIG. 7. Separation of Mg(II) from Ca(II) and of Hg(II) from Pb(II) on antimony(V) silicate columns: (a), 0.1 *M* $HClO_4$; (b) and (d), 1 *M* $HClO_4$; (c) 10% HCl + 5% DMSO.

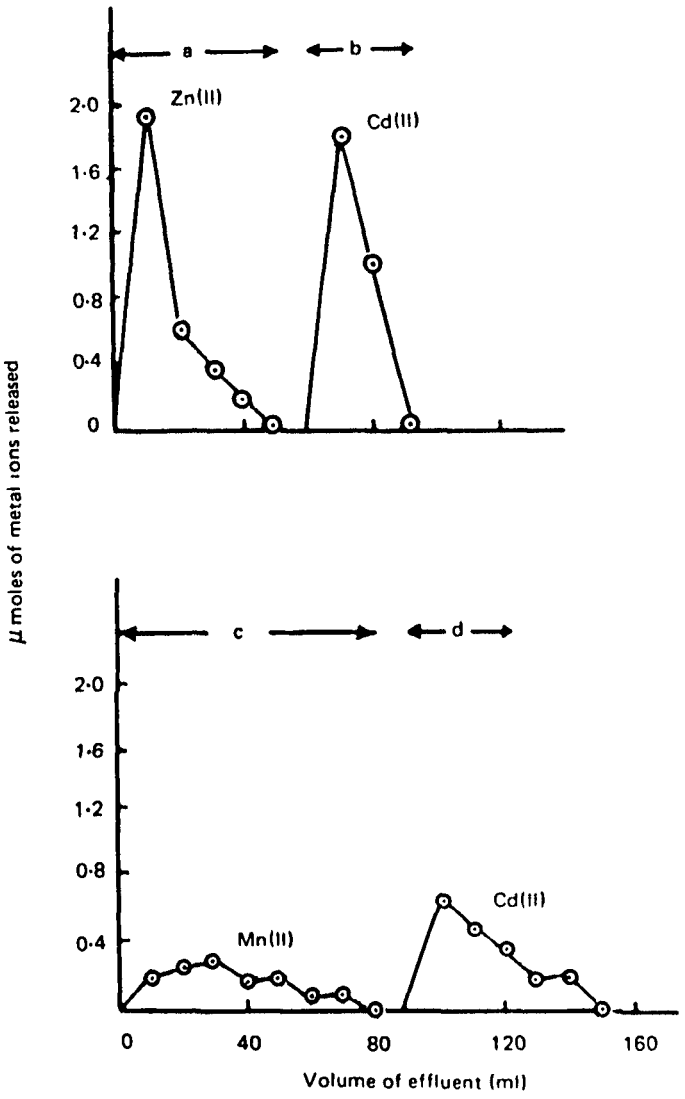


FIG. 8. Separation of Cd(II) from Zn(II) and of Mn(II) on antimony(V) silicate columns (a) and (c), 0.1 *M* $HClO_4$; (b) and (d), 1 *M* $HClO_4$

TABLE 6
Binary Separations Achieved on Antimony(V) Silicate Columns

Sample	Separations achieved (M_1–M_2)	Amount taken (μg)		Amount found (μg)		Error (%)		Eluent and its volume used for different metals
		M_1 (μg)	M_2 (μg)	M_1 (μg)	M_2 (μg)	M_1	M_2	
1	Zn–Cd	200.0	304.0	204 0	309.0	0 0	+1.6	Zn: 0.1 *M* $HClO_4$, 50 mL Cd: 1 *M* $HClO_4$, 30 mL
2	Mn–Cd	71.0	187.0	67 0	187 0	−5.6	0.0	Mn: 0.1 *M* $HClO_4$, 80 mL Cd: 1 *M* $HClO_4$, 60 mL
3	Hg–Pb	240.0	517 0	240 0	497.0	0 0	−3.8	Hg: 10% HCl + 5% DMSO, 40 mL Pb: 1 *M* $HClO_4$, 40 mL
4	Mg–Ca	34 0	64 0	35 0	64 0	−2.6	0.0	Mg: 0.1 *M* $HClO_4$, 70 mL Ca: 1 *M* $HClO_4$, 50 mL
5	Mg–Ba	34 0	112.0	34 0	112.0	0 0	0 0	Mg. 0.1 *M* $HClO_4$, 50 mL Ba 1 *M* $HClO_4$, 60 mL
6	Mg–Sr	48 0	123 0	49 0	123 0	−2 0	0 0	Mg 0 1 *M* $HClO_4$, 80 mL Sr 1 *M* $HClO_4$, 20 mL

Acknowledgments

The authors thank Prof Mohsin Qureshi for research facilities and Dr M. Sankar Das (Head, Analytical Chemistry Division, Bhabha Atomic Research Centre, Bombay) for the radiotracer facilities The financial assistance provided by the C.S.I.R. (India) is gratefully acknowledged

REFERENCES

1 D Naumann, *Kernenergie, 6*, 173 (1963)
2 S J Naqvi, D Huys, and L H Baetsle, *J Inorg Nucl Chem 33*, 4317 (1971)
3 K G Varshney and A Premadas, *J Liq Chromatogr, 4* 915 (1981)
4 K G Varshney and A Premadas, *Ibid, 4*, 1247 (1981)
5 A N Lapitskii and V F Tikavyi, *Zh Khim, 2*, 19 (1969) (in Russian)
6 A N Lapitskii and V F Tikavyi, *Ser Khim Navuk, 5*, 57 (1971) (in Russian)
7 M Qureshi and V Kumar, *J Chromatogr, 62* 431 (1971)
8 M Qureshi and Y Kumar, *Ibid, 67*, 351 (1972)
9 B G Novikov, F A Belinskaya, and E A Materova *Fiz Khim 1* 29 (1971) (in Russian)
10 B G Novikov, F A Belinskaya, and E A Materova, *Ibid, 1*, 35 (1971) (in Russian)
11 B G Novikov, F A Belinskaya, and E A Materova, *Otkrit Izobret, Prom Obraz, Tovar Znaki, 48*, 71 (1971)
12 B G Novikov, F A Belinskaya, and E A Materova *Fiz Khim, 1*, 94 (1976) (in Russian)
13 B G Novikov, F. A. Belinskaya, and E A Materova, *Ionnyi Obmen, Lenometriya, 1*, 66 (1976) (in Russian)
14 K G Varshney and A A Khan, *J Inorg Nucl Chem, 41*, 241 (1978)
15 I M Kolthoff and E B Sandell, *Text Book of Quantitative Inorganic Analysis* Macmillan New York, 1938, p 383
16 W W Scott, *Standard Methods of Chemical Analysis* 5th ed Van Nostrand New York 1939, p 74
17 N H Furman, *Standard Methods of Chemical Analysis*, 6th ed, Van Nostrand New York, 1962, p 83
18 W W Scott, *Standard Methods of Chemical Analysis* 5th ed Van Nostrand New York 1939, p 803
19 N E Topp and K W Pepper, *J Chem Soc*, p 3299 (1949)
20 C M Reilley, R W Schmid and Fawzy, *J Chem Educ 36* 555 (1959)
21 K G Varshney and A Premadas, *Sep Sci Technol, 16*, 793 (1981)
22 K G Varshney, S Naheed, A A Khan, S N Tandon, and C B Gupta, *Chromatographia, 12*, 473 (1979)
23 M Abe and I Ito, *Bull Chem Soc Jpn, 41*, 333 (1968)
24 M Abe and K Uno, *Sep Sci Technol, 14*, 355 (1979)
25 J A Gadsden *Infrared Spectra of Minerals and Related Inorganic Compounds* Acford Sussex, 1975, p 36

Received by editor January 8, 1982
Revised May 5, 1982

66

2.7

Crystalline Zirconium(IV) Hydrogenarsenate Hydrogenphosphate Monohydrate: Synthesis, Ion-exchange Properties, and Thermal Behaviour

Maria L. Berardelli, Paola Galli, and Aldo. La Ginestra*
Dipartimento di Chimica, Università di Rome, Rome, Italy
Maria A. Massucci
Istituto di Metodologie Avanzate Inorganiche del C.N.R., Area della Ricerca di Roma, C.P. 10 Monterotondo Scalo, Rome, Italy
Krishna G. Varshney
Department of Chemistry, Aligarh Muslim University, Aligarh, India

A new crystalline layered inorganic ion-exchanger with formula $Zr(HAsO_4)(HPO_4)\cdot H_2O$ has been prepared by refluxing the amorphous product. Its ion-exchange properties towards sodium ions and its thermal behaviour, together with that of the pure sodium phases obtained, are reported and discussed. The exchanger is very stable to hydrolysis and has a high exchange capacity. Its general behaviour is intermediate between that of $Zr(HPO_4)_2\cdot H_2O$ and $Zr(HAsO_4)_2\cdot H_2O$.

In recent years synthetic inorganic ion-exchangers of the class of acid phosphates or arsenates of tetravalent metals, with general formula $M(HEO_4)_2\cdot nH_2O$ (M = Ge, Ti, Zr, or Sn; E = P or As; n = 1, 2, *etc.*) have received increasing attention because of their potential employment in catalysis.[1-4]

In our investigation on the catalytic properties of zirconium(IV) hydrogenphosphate and other members of the class of crystalline layered materials, we have observed that for a given test reaction, their activity depends on the chemical compound, the degree of crystallinity, the structure of the phase present during the catalytic process, the thermal pre-treatment, surface area, *etc.*[5]

Since until now only 'single' salts have been investigated in this field, we were interested in studying the catalytic behaviour of 'mixed' materials [*i.e.* compounds containing two different tetravalent metals and a given anion (phosphate or arsenate) or two different anions and a given tetravalent metal], in order to determine how the gradual substitution of one tetravalent metal with another or one pentavalent element with another affects the catalytic activity of these materials.

Examples of mixed compounds are the crystalline zirconium–titanium phosphates with different compositions[6] and the amorphous arsenate phosphates of tetravalent metals,[7,8] studied merely as ion-exchangers.

The mixed zirconium–titanium acid phosphates were prepared by Clearfield and Frianeza[6] in an attempt to obtain pure phases with a controlled ion-sieve efficiency and to improve the poor stability towards hydrolysis of the single α-titanium acid phosphate, $\alpha\text{-}Ti(HPO_4)_2\cdot H_2O$.

The amorphous arsenate phosphates of Ti, Zr, Sn, and Ce proved to be interesting for their selective ion-exchange properties. For the amorphous zirconium arsenate phosphate, with molar ratio Zr:As:P = 1:1:1, Varshney and co-workers[7,8] found that its ion-exchange capacity, rather low if compared to those of the layered crystalline acid phosphates, is maintained to some extent after ignition at 800 °C. The material is severely hydrolyzed in slightly alkaline media.[7]

In this paper we report the preparation, the ion-exchange behaviour towards sodium ions, and the chemical stability of the crystalline zirconium arsenate phosphate of formula $Zr(HAsO_4)(HPO_4)\cdot H_2O$, together with phase changes with temperature, with a view to its subsequent employment in catalysis. Comparisons with the single salts $\alpha\text{-}Zr(HPO_4)_2\cdot H_2O$ and $\alpha\text{-}Zr(HAsO_4)_2\cdot H_2O$ are also made.

Table 1. Analytical data for crystalline zirconium(IV) hydrogenarsenate hydrogenphosphate monohydrate

	Analysis (%)			
	ZrO_2	P_2O_5	As_2O_5	H_2O
Found for four representative preparations	35.65	20.65	33.30	10.40
	35.70	20.65	33.45	10.20
	35.70	20.50	33.30	10.50
	35.60	20.50	33.30	10.60
Calculated*	35.65	20.60	33.35	10.45

* Calculated for $ZrO_2(As_2O_5)_{0.5}(P_2O_5)_{0.5}\cdot 2H_2O$.

Experimental

Chemicals.—All reagents were Erba RPE-ACS products except $ZrOCl_2\cdot 8H_2O$, which was a Merck 'pro analysi' product.

Preparation of $\alpha\text{-}Zr(HAsO_4)_2\cdot H_2O$ *and* $\alpha\text{-}Zr(HPO_4)_2\cdot H_2O$. Crystalline zirconium(IV) hydrogenphosphate, $Zr(HPO_4)_2\cdot H_2O$, and hydrogenarsenate, $Zr(HAsO_4)_2\cdot H_2O$, were prepared as described[9,10] by refluxing the amorphous product in 10 mol dm^{-3} H_3PO_4 and 4 mol dm^{-3} H_3AsO_4 respectively, for 100 h. These preparations will be referred to throughout as (10,100) and (4,100) respectively, the first number in each case indicating the acid concentration and the second the reflux time.

Preparation of Crystalline Zirconium(IV) *Hydrogenarsenate Hydrogenphosphate.*—A solution (volume 500 cm^3) containing $ZrOCl_2\cdot 8H_2O$ (50 g) was added under stirring at room temperature to a 500-cm^3 solution containing 14.5 mol dm^{-3} H_3PO_4 (12 cm^3) and $3As_2O_5\cdot 5H_2O$ (40 g): a white gel immediately formed. The slurry to which was added 14 mol dm^{-3} HNO_3 (88 cm^3) was refluxed for 50 h; then, to help the crystallization process, the suspension was made 4 mol dm^{-3} in HNO_3 and refluxed for a further 50 h. After cooling, the solid was filtered off, washed with water till pH 4.5, and dried over P_4O_{10} under vacuum to constant weight.

Analytical data for four preparations of this crystalline product are summarized in Table 1 and show it to have the stoicheiometry $ZrO_2(As_2O_5)_{0.5}(P_2O_5)_{0.5}\cdot 2H_2O$. The first mole of water is lost by 150 °C, the second after heating at 700 °C.

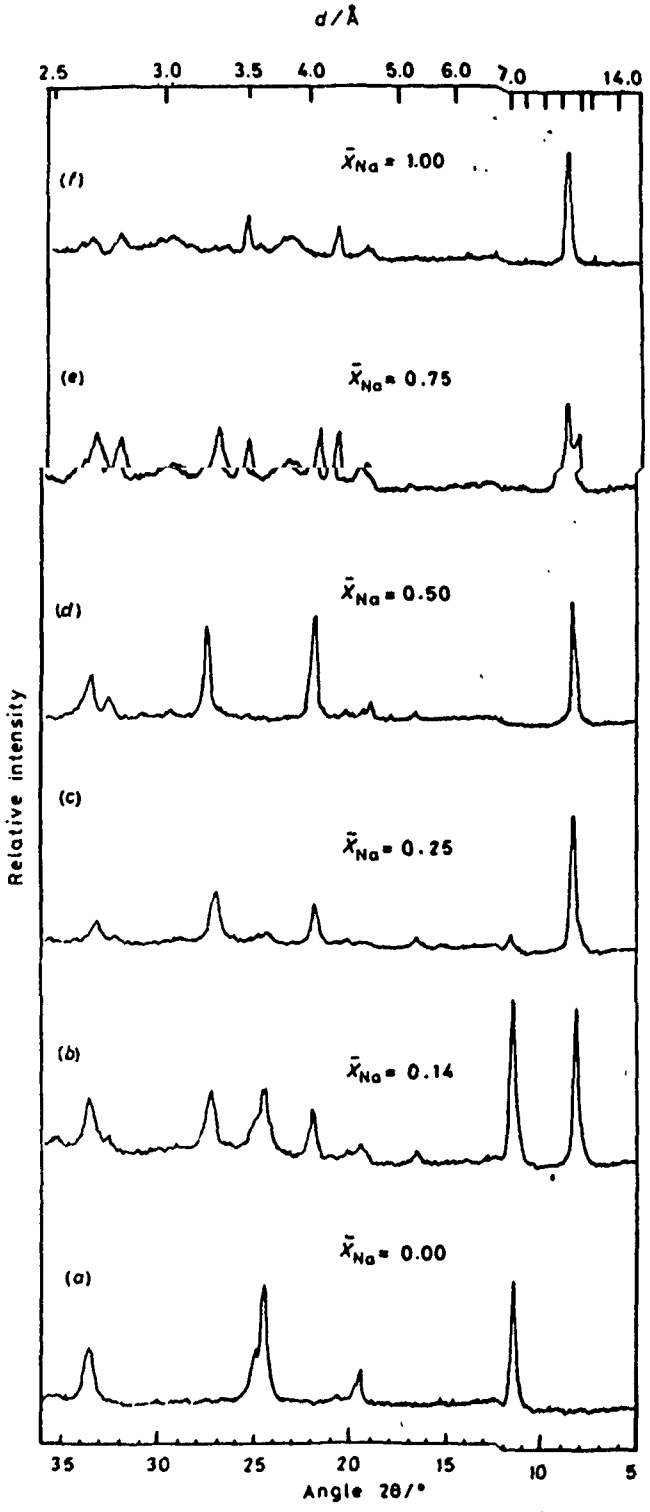


Figure 1. *X*-Ray diffraction patterns of samples at different Na^+ loadings, expressed in molar fraction of sodium content in the solid ($\bar{X}_{Na}$)

Titration Curve.—The titration of $Zr(HAsO_4)(HPO_4)\cdot H_2O$ was carried out by the batch procedure, equilibrating several samples of exchanger (0.5 g) with 100 cm^3 of a 0.1 mol dm^{-3} (NaCl + NaOH) solution. In the range 70—100% conversion, the last amounts of titrant were added at intervals to prevent hydrolysis. After shaking at 20 °C for 3 d, the supernatant liquids were filtered off, analyzed for their arsenate and phosphate content, and their pH measured.

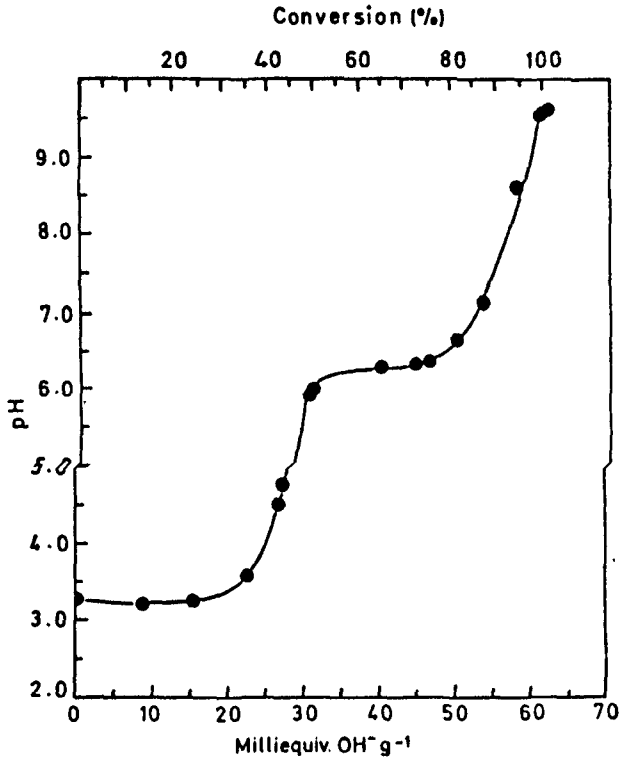


Figure 2. Titration-uptake curve for $Zr(HAsO_4)(HPO_4)\cdot H_2O$: titrant 0.1 N NaOH + 0.1 N NaCl

Analytical Procedures and Physical Measurements.—The Zr:As:P ratio of crystalline $Zr(HAsO_4)(HPO_4)\cdot H_2O$ was determined as follows. 300 mg of material were dissolved in 1 mol dm^{-3} HF (10 cm^3) and the solution diluted to 50 cm^3. Zirconium was determined gravimetrically as described [11] in 10 cm^3 of this solution. Arsenate was determined iodometrically in 10 cm^3 of solution. Phosphate was determined colorimetrically as described,[12] in 2 cm^3 of solution. Since the method is also valid for the determination of arsenate, in order to subtract the unavoidable positive interference of this ion, the measurements were made against a reference solution containing the amount of arsenate present in the same volume, previously determined. A photoelectron DL spectrophotometer was used.

The same methods were employed for the determination of arsenate and phosphate present in the supernatant liquids of the batch-titration.

The solids (at various degrees of exchange) obtained from the titration were washed and conditioned over saturated $BaCl_2$ solution at 20 °C ($p/p_0 \simeq 0.9$).

X-Ray diffraction patterns were taken on a Philips PW 1130 diffractometer using nickel-filtered Cu-K_α radiation.

The water content of $Zr(HAsO_4)(HPO_4)\cdot H_2O$, and of the pure phases formed during the titration, was determined from the weight losses during heating up to 900 °C.

Thermogravimetric (t.g.) and differential thermal analysis (d.t.a.) measurements were carried out on a Stanton simultaneous thermoanalyzer, model STA 781, with a heating rate of 5 °C min^{-1}, Pt/Pt–Rh (87 : 13) thermocouples, and platinum crucibles.

Results and Discussion

Although the structure of the new compound is not known, its *X*-ray powder diffraction pattern shown in Figure 1(*a*) (the corresponding *d* values are listed in Table 2) shows a great similarity with those of α-$Zr(HPO_4)_2\cdot H_2O$ [13] and α-Zr(HAs-

Table 2. *X*-Ray powder diffraction spectra of the $ZrH_2(AsO_4)(PO_4)$ forms and their dehydration products

$ZrH_2(AsO_4)(PO_4)\cdot H_2O$[a]		Layered $ZrAsPO_7$[b]		Cubic $ZrAsPO_7$[c]		$ZrH_2(AsO_4)(PO_4)\cdot nH_2O$[d]	
d/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%
7 73	100	6 23	46	4 83	14	10 64	100
4 56	25	4 52	31	4 19	100	5.52	8
4 50	14	4 36	77	3.74	50	5.37	5
4 30	5	3.70	100	3.41	43	4.78	13
3 62	89	3.14	23	2.96	27	4.50	15
3 56	42	2.68	54	2.52	45	4.30	30
2 67	44	2.60	31	2.31	13	4.21	28
2 53	5					3.81	37
2 43	11					3.49	45
2 37	5					3.40	37
2 13	7					3.07	18
2 06	5					2.90	7
1 90	11					2.81	8
1 89	10					2.77	23
1 80	7					2.71	18
						2 67	28
						2.52	8
						2.41	5
						2.36	5

[a] Dried over P_4O_{10}. [b] After heating at 650 °C. [c] After heating at 800 °C. [d] As prepared.

Table 3. *X*-Ray powder diffraction spectra of sodium half-exchanged $ZrH_2(AsO_4)(PO_4)\cdot H_2O$ and its dehydration products

$ZrHNa(AsO_4)(PO_4)\cdot 4H_2O$[a]		$ZrHNa(AsO_4)(PO_4)\cdot H_2O$[b]		$ZrHNa(AsO_4)(PO_4)$[c]		$NaZr_2(As_{0.5}P_{0.5}O_4)_3$[d]	
d/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%
10 71	100	8 00	80	7.19	50	6 46	48
5 30	8	4 40	43	4 64	10	4 63	44
4 65	16	4 21	100	4 41	10	4 49	46
4 55	10	3 86	8	4 03	25	3 87	100
4 36	8	3 55	71	3 95	37	3 22	47
4 23	5	3 33	26	3 85	100	2 91	100
4 03	86	3 19	91	3 26	15	2 60	21
3 52	5	2 97	18	2 85	37	2 59	46
3 25	78	2 86	14	2.79	37	2 31	5
3 03	5	2 81	14	2 59	25	2 21	12
2 74	17	2.73	48			2 14	5
2 66	35	2 59	51			2 11	5
2 46	5					2 05	21
2 40	8					2 01	10
2 17	8					1.97	7
2 10	8					1 95	3
						1.93	31

[a] Conditioned at 90% relative humidity. [b] Dried over P_4O_{10}. [c] After heating at 300 °C. [d] After heating at 700 °C.

$O_4)_2\cdot H_2O$.[14] These data together with the ion-exchange and thermal behaviour given below, strongly support the hypothesis that the material possesses an α-type layered structure. As a consequence, we assign the new compound the formula $Zr(HAsO_4)(HPO_4)\cdot H_2O$ and assume the first *d* value of 7.73 Å as the distance between two adjacent planes of zirconium atoms (d_{002}).

Ion-exchange Properties of Crystalline $Zr(HAsO_4)(HPO_4)\cdot H_2O$ *towards Sodium Ions.*—Figure 2 shows the titration and uptake curves for the $Na^+ \longrightarrow \bar{H}^+$ process.* The curves are practically coincident since only negligible amounts of arsenate and phosphate ions were found in the solutions below pH 10. All data refer to 1 g of exchanger.

The titration process occurs in two stages, each stage requiring *ca.* 2 95 milliequiv. of OH^- ions. The total amount of NaOH employed (5.85 milliequiv.) is in good agreement with the theoretical ion-exchange capacity of the exchanger (5.80 milliequiv. g^{-1}) calculated by considering two exchangeable hydrogens per mole formula.

X-Ray patterns of the samples at various degrees of Na^+ uptake (Figure 1) completely agree with the shape of the titration curve. In the plateaux (constant pH 3.3 and 6 3 respectively) two phases are present, while along the slopes only one phase is found, in agreement with the phase rule.[15] Up to 3% Na^+ uptake, the solid maintains the structure of the dihydrogen form, then, in the range of 4—30% Na^+ loading, a new phase with an interlayer distance of 10 64 Å co-exists with the phase at d_{002} = 7.73 Å, the former increasing and the latter decreasing in intensity with Na^+ uptake [Figure 1(*b*) and (*c*)]. At the end of the plateau (≃30% of Na^+ exchanged) only the '10 64 Å' phase is present. The subsequent sodium uptake up to 50% occurs with the formation of a solid solution since no other phases appear: the interlayer distance of the phase present gradually shifts from 10 64 to 10.71 Å.

* $Na^+ \longrightarrow \bar{H}^+$ represents Na^+ replacing H^+ in the exchanger.

Table 4. *X*-Ray powder diffraction spectra of sodium full-exchanged $ZrH_2(AsO_4)(PO_4)\cdot H_2O$ and its dehydration products

$ZrNa_2(AsO_4)(PO_4)\cdot 3H_2O$[a]		$ZrNa_2(AsO_4)(PO_4)\cdot H_2O$[b]		$ZrNa_2(AsO_4)(PO_4)$[c]	
d/Å	*I*/%	*d*/Å	*I*/%	*d*/Å	*I*/%
9.93	100	9.76	100	7.10	20
4.52	9	7.89	7	4.60	15
4.20	29	4.50	15	4.48	14
3.76	13	4.18	47	4.38	22
3.53	9	3.74	20	3.95	100
3.44	38	3.52	4	3.86	30
3.30	7	3.42	38	3.21	15
2.96	13	3.27	4	3.16	22
2.74	20	3.21	4	2.97	90
2.63	13	2.97	20	2.91	35
2.59	9	2.72	23	2.64	45
		2.61	25	2.60	17
				2.27	7
				1.97	35

[a] Conditioned at 90% relative humidity. [b] Dried over P_4O_{10}. [c] After heating at 700 °C.

At 50% Na^+ conversion the phase has the composition $ZrHNa(AsO_4)(PO_4)\cdot 4H_2O$. Its *X*-ray pattern is shown in Figure 1(*d*), while the *d* values are reported in Table 3.

The same reasoning applies between 50 and 100% of exchange Here the new phase, possessing an interlayer distance of 9.93 Å, co-exists with the half-sodium form until at *ca.* 85% Na^+ loading [Figure 1(*e*)]; after this point it is the only one present At the end of the process the new phase, still with d_{002} = 9.93 Å, has a composition $ZrNa_2(AsO_4)(PO_4)\cdot 3H_2O$ since the degree of hydrolysis is negligible. Its *X*-ray diffraction pattern is shown in Figure 1(*f*) and the corresponding *d* values are reported in Table 4.

The ion-exchange behaviour of $Zr(HAsO_4)(HPO_4)\cdot H_2O$ towards sodium ions is very similar to that found on titrating α-$Zr(HAsO_4)_2\cdot H_2O$ (4,100)[10] and α-$Zr(HPO_4)_2\cdot H_2O$(10,100),[16] the only difference is that the new exchanger exhibits shorter plateaux and wider slopes.

It is known that, for a given exchanged cation, the shape of the titration curve for these layered materials depends on the degree of crystallinity:[17,18] the lower the degree of crystallinity, the shorter is the plateau and therefore the wider is the step involving the solid solution formation (slope).[18,19]

In order to obtain information on the degree of crystallinity of $Zr(HAsO_4)(HPO_4)\cdot H_2O$, the procedure of Alberti *et al.*[20] was employed. These authors found that the back-titration of the half-sodium form of the α-$Zr(HPO_4)_2\cdot H_2O$ with the highest degree of crystallinity restores the monohydrated dihydrogen form, $Zr(HPO_4)_2\cdot H_2O$ (d_{002} = 7.56 Å), while zirconium(IV) hydrogenphosphates with gradually decreasing crystallinities give mixtures of a '7.56 Å phase,' and $Zr(HPO_4)_2\cdot 6H_2O$ (d_{002} = 10.4 Å) (termed θ-ZP by Clearfield *et al.*[21]), or $Zr(HPO_4)_2\cdot 6H_2O$ and a hydrogen phase with d_{002} = 11.5 Å. Pure $Zr(HPO_4)_2\cdot 6H_2O$ was obtained from the half-sodium form of α-$Zr(HPO_4)\cdot H_2O$ (10,100), which has a medium-to-low degree of crystallinity. This procedure applied on $Zr(HAsO_4)(HPO_4)\cdot H_2O$ and α-$Zr(HAsO_4)_2\cdot H_2O$ (4,100) gave pure dihydrogen forms $Zr(HAsO_4)(HPO_4)\cdot nH_2O$ and $Zr(HAsO_4)_2\cdot nH_2O$ ($n \gg 1$) respectively. Left in air, the materials lose water and the monohydrated dihydrogen forms are rapidly re-obtained as for $Zr(HPO_4)_2\cdot 6H_2O$. The *d* values of the highly hydrated $Zr(HAsO_4)(HPO_4)$ are given in Table 2.

From these experiments, it can be supposed that $Zr(HAsO_4)(HPO_4)\cdot H_2O$, prepared by refluxing the amorphous product for 100 h, should possess a degree of crystallinity comparable to that of α-$Zr(HPO_4)_2\cdot H_2O$ (10,100) and α-$Zr(HAsO_4)_2\cdot H_2O$ (4,100).

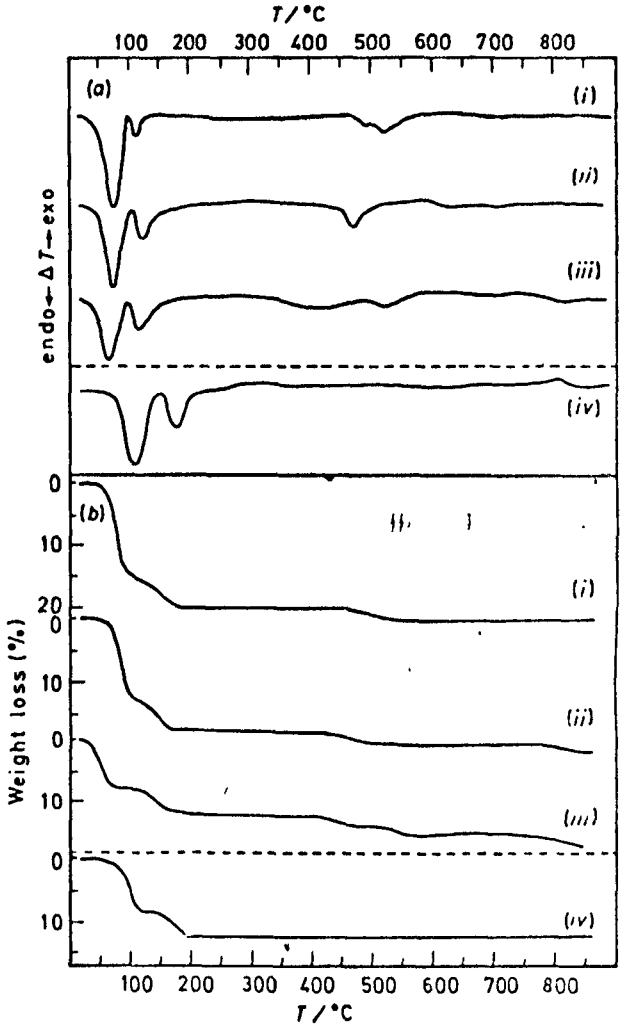


Figure 3. (*a*) D.t.a. and (*b*) t.g. curves of (*i*) $ZrH_2(PO_4)_2\cdot H_2O$, (*ii*) $ZrH_2(AsO_4)(PO_4)\cdot H_2O$, (*iii*) $ZrH_2(AsO_4)_2\cdot H_2O$, and (*iv*) $ZrH_2(AsO_4)(PO_4)\cdot nH_2O$ (regenerated)

Thus the shorter plateaux and wider slopes observed in the titration curve of $Zr(HAsO_4)(HPO_4)\cdot H_2O$ could be due either to the low degree of crystallinity or to a greater tendency of the mixed exchanger to give solid solutions because of the presence

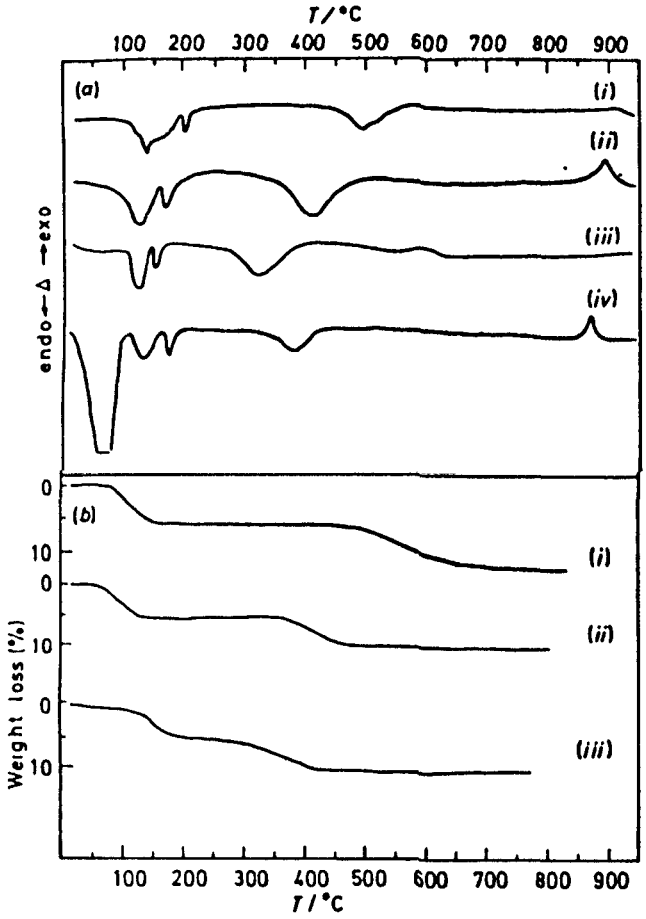


Figure 4. (*a*) D t a and (*b*) t g curves of (*i*) $ZrHNa(PO_4)_2 \cdot 5H_2O$, (*ii*) $ZrHNa(AsO_4)(PO_4) \cdot 4H_2O$, (*iii*) $ZrHNa(AsO_4)_2 \cdot 3H_2O$, and (*iv*) $ZrNa_2(AsO_4)(PO_4) \cdot 3H_2O$

in the lattice layer of atoms (P and As) with analogous chemical characteristics but different dimensions.

Thermal behaviour of $Zr(HAsO_4)(HPO_4) \cdot H_2O$ *and the Sodium-exchanged Phases*—In order more completely to characterize the new ion-exchanger, the thermal behaviour of the dihydrogen and sodium forms of $Zr(HAsO_4)(HPO_4) \cdot H_2O$ was studied and the results compared with those for the corresponding α-$Zr(HPO_4)_2 \cdot H_2O$ and α-$Zr(HAsO_4)_2 \cdot H_2O$ phases

Figure 3 shows the t g and d t a curves obtained from $ZrH_2(AsO_4)(PO_4) \cdot H_2O$, $ZrH_2(AsO_4)_2 \cdot H_2O$, and $ZrH_2(PO_4)_2 \cdot H_2O$ $ZrH_2(AsO_4)(PO_4) \cdot H_2O$ loses the mole of hydration water in the range 40—150 °C, and the related endothermic effect is narrower than those of $ZrH_2(AsO_4)_2 \cdot H_2O$ and $ZrH_2(PO_4)_2 \cdot H_2O$. The second endothermic effect (which is connected with a reversible phase transition) is thus better resolved than in the case of the other two exchangers [22] It must be pointed out that in the case of $ZrH_2(AsO_4)(PO_4) \cdot H_2O$ the phase transition occurs on the anhydrous phase, whilst for the other two materials it occurs on not completely dehydrated phases

The third endothermic effect is related to the condensation of the ≡As–OH and ≡P–OH groups and the process takes place in the range 340—470 °C. The analogous processes for $ZrH_2(AsO_4)_2$ *and* $ZrH_2(PO_4)_2$ *occur in the ranges 300—370 and* 450—600 °C, respectively. Therefore, the thermal stability of these dihydrogen phases decreases as the phosphate groups are substituted with the arsenate ones.

After the condensation process, a layered zirconium pyroarsenophosphate is formed; above 800 °C, this transforms into a cubic pyro-compound (Table 2) behaving in exactly the same fashion as do $ZrH_2(PO_4)_2 \cdot H_2O$ and the other layered exchangers of this class.[23]

Figure 4 shows the t.g. and d.t.a. curves of $ZrHNa(AsO_4)(PO_4) \cdot 4H_2O$, together with those of $ZrHNa(AsO_4)_2 \cdot 3H_2O$ and $ZrHNa(PO_4)_2 \cdot 5H_2O$ for comparison.

The three half-exchanged materials lose their hydration water between 40 and 200 °C. The process occurs in two steps. The first weight loss leads to monohydrated phases, the second to anhydrous phases. Each monohydrated or anhydrous phase possesses a well defined interlayer spacing, which decreases with the decreasing water content.

The *X*-ray diffraction analysis shows that below 400 °C, all the materials maintain the layered structure. For the $ZrHNa(AsO_4)(PO_4)$ forms, d_{002} varies from 10.71 Å for the *tetrahydrated compound, to 7.19 Å for the anhydrous phase* heated at 300 °C.

In the range 400—500 °C, $ZrHNa(AsO_4)(PO_4)$ undergoes the condensation process. At 500 °C the solid is amorphous, then, at *ca.* 600 °C (after the occurrence of the exothermic peak in the d.t.a. curve) a recrystallization takes place with the formation of a new phase, isostructural with $NaZr_2(PO_4)_3$ and $NaZr_2(AsO_4)_3$ obtained by heating $ZrHNa(PO_4)_2$[24] and $ZrHNa(AsO_4)_2$[25] at 650 °C. The new phase should correspond to a sodium dizirconium tris(arsenate phosphate) with formula $NaZr_2(As_{0.5}P_{0.5}O_4)_3$.

The *X*-ray patterns of the various phases obtained from $ZrHNa(AsO_4)(PO_4) \cdot 4H_2O$ are reported in Table 3.

The t g. and d t a. curves of $ZrNa_2(AsO_4)(PO_4) \cdot 3H_2O$ are also shown in Figure 4 The dehydration process is quite similar to that observed in the case of $ZrNa_2(PO_4)_2 \cdot 3H_2O$.[24] The three moles of water are lost in two steps: two moles between 50 and 150 °C and the last mole between 150 and 200 °C. From 200 up to 780 °C, neither weight losses nor other phenomena are observed and the solid maintains the layered structure At *ca.* 850 °C, after the occurrence of an exothermic peak in the d t a. curve, besides the layered phase, a new phase begins to form, the evolution of which cannot be followed because the material decomposes after 950 °C, with gradual elimination of As_2O_5

The *X*-ray patterns of the various phases obtained from $ZrNa_2(AsO_4)(PO_4) \cdot 3H_2O$ are given in Table 4.

Conclusions

It is possible to prepare reproducibly, as a single crystalline phase, a layered mixed inorganic ion-exchanger containing two anions in a 1:1 ratio, *i.e.* $Zr(HAsO_4)(HPO_4) \cdot H_2O$, which is isostructural with $Zr(HPO_4)_2 \cdot H_2O$ and $Zr(HAsO_4)_2 \cdot H_2O$, and posseses an interlayer spacing of 7.73 Å, intermediate between those of the last two compounds

We believe that obtaining a single phase with the least favourable molar ratio (As: P = 1:1) presumably indicates that the Zr arsenate phosphate system shows a wide, if not complete, miscibility.

The substitution of P with As allows not only the variations in the ion-exchange and thermal properties of these materials to be gradually followed, but also the strength of their acidic sites when employed as acid catalysts. A study in this area is in progress [5]

References

1 F Nozaki, T Itoh, and S Ueda, *Nippon Kagaku Kaishi*, 1973, 4, 474
2 T Kalman and A Clearfield, *Proc. 3rd Int. Symp. Chem. React Eng Adv Chem*, 3rd Series, 1974, 65, 133.
3 A Clearfield and D S Thakur, *J. Catal.*, 1980, 65, 185.
4 M. Iwamoto, Y. Nomura, and S. Kagawa, *J. Catal*, 1981, 69, 234.

5 A. La Ginestra, P. Patrono, M. L. Bernardelli, P. Galli, M. A. Massucci, C. Ferragina, and P. Ciambelli, XVII Congresso Nasionale di Chimica Inorganica, October 1984, Cefalù, Italy.
6 A Clearfield and T N Frianeza, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1925.
7 K. G Varshney and A. Premadas, *Sep. Sci. Technol.*, 1981, **16**, 793.
8 K. G Varshney and A. A. Khan, *J. Inorg. Nucl. Chem.*, 1979, **41**, 241.
9 G Alberti, U. Costantino, S. Allulli, and M. A. Massucci, *J. Inorg. Nucl Chem*, 1973, **38**, 1339.
10 E Torracca, U. Costantino, and M. A. Massucci, *J. Chromatogr.*, 1967, **30**, 584
11 G Alberti, A Conte, and E Torracca, *J. Inorg. Nucl. Chem.*, 1966, **28**, 225
12 D. N Bernhart and A. R Wreath, *Anal. Chem.*, 1955, **27**, 440.
13 A Clearfield and Y. D Smith, *Inorg. Chem.*, 1969, **8**, 431.
14 A Clearfield and W. L. Duax, *Acta Crystallogr., Sect. B*, 1969, **25**, 2658
15 A Clearfield, W L. Duax, J. M. Garces, and A. S. Medina, *J. Inorg. Nucl Chem*, 1973, **34**, 329
16 G Alberti, S Allulli, U Costantino, P. Galli, M. A. Massucci, R Platania, and E Torracca, 2nd Symposium on Ion Exchange, ed. J. A. Mikes, Magyar, Budapest, 1969, vol. 1.
17 A. Clearfield, in 'Inorganic Ion Exchange Materials,' ed A. Clearfield, CRC Press Inc., Boca Raton, Florida, 1981, ch. 1.
18 G Alberti, U. Costantino, S. Allulli, M. A. Massucci, and M. Pelliccioni, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1347.
19 A. Clearfield, Å. Oskarsson, and C. Oskarsson, *Ion Exch. Membr.*, 1972, **1**, 9.
20 G. Alberti, U. Costantino, and J. S. Gill, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1783.
21 A. Clearfield, A. L. Landis, A. S. Medina, and J. M. Troup, *J. Inorg. Nucl. Chem*, 1973, **35**, 1099.
22 A. La Ginestra, C. Ferragina, M. A. Massucci, and N. Tomassini, *Proc. 3rd Int. Conf. Therm. Anal.*, Akadémiai Kiadó, Budapest, 1974, **1**, 631.
23 U. Costantino and A. La Ginestra, *Thermochim. Acta*, 1982, **58**, 179.
24 A. Clearfield, W. L. Duax, A. S. Medina, G. D Smith, and J. R. Thomas, *J. Phys. Chem.*, 1969, **73**, 3424.
25 G. Alberti, U. Costantino, and M. A. Massucci, unpublished work.

Received 2nd *July* 1984; *Paper* 4/1129

SEPARATION SCIENCE AND TECHNOLOGY, 16(7), pp. 793-803, 1981

34

2.8 Synthesis, Composition, and Ion-Exchange Behavior of Thermally Stable Zr(IV) and Ti(IV) Arsenophosphates: Separation of Metal Ions

K. G. VARSHNEY and A. PREMADAS

CHEMISTRY SECTION
Z. H. COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH 202001, INDIA

Abstract

Two new inorganic ion-exchange materials, Zr(IV) and Ti(IV) arsenophosphates, have been synthesized. They are reproducible in behavior and possess excellent thermal stability. Their tentative structures have been proposed based on pH titrations, thermogravimetry, chemical analysis, IR studies, and other ion-exchange properties. Distribution studies of some metal ions have also been made on the basis of which several useful binary separations have been achieved such as Fe(III) from VO(II), Cu(II), and Zn(II); Pb(II) from Cu(II), Hg(II), and Zn(II); Ti(IV) from UO_2(II) and Ce(IV); and Mg(II) from Sr(II) and Ba(II).

INTRODUCTION

Inorganic ion exchange materials (*1*) are important for metal separations. Double salts show some peculiar characteristics over their single salt counterparts. Zirconium phosphosilicate (*2*), for example, has successfully been used for plutonium isolation, and titanium phosphosilicate (*3*) for the separation of radionuclides. Stannic vanadophosphate (*4*) and stannic arsenophosphate (*5–7*) possess appreciable ion-exchange capacity even at elevated temperatures. The present work is in continuation of our studies on the double salts as inorganic ion exchangers. Two new arsenophosphates of zirconium and titanium have been synthesized which possess high thermal and chemical stability. Also, some important binary metal separations have been achieved on their columns.

EXPERIMENTAL

Reagents

Zirconyl chloride used in this study was a product of J. T. Baker Chemical Co. (Phillipsburg, New Jersey). Titanic chloride (sp. gr. 1.73), ammonium ceric sulfate, and trisodium orthophosphate were obtained from the B.D.H. Poole (England), while disodium arsenate was an E. Merck (Darmstadt) product. All other reagents and chemicals were of AnalaR grade.

Apparatus

pH measurements were made on an Elico (India) model LI-10, while IR studies were performed on a Perkin-Elmer 621 Grating Infrared Spectrophotometer using a nujol phase. A temperature-controlled Sico (India) shaker was used for shaking purposes, and the TGA apparatus was from FCI (India). A Bausch and Lomb spectronic 20 colorimeter was used for the spectrophotometric studies.

Preparation of Reagent Solutions

A stock solution (1 *M*) of titanic chloride was prepared in a 30% HCl solution which was diluted to the desired concentration with demineralized water (DMW). Zirconyl chloride, ceric ammonium sulfate, disodium arsenate, and trisodium orthophosphate were dissolved in DMW directly. The metal ion solutions for the distribution studies were also prepared in DMW except for trivalent and tetravalent metals for which 2–3 drops of the corresponding acids were added to prevent hydrolysis.

Synthesis of the Ion-Exchange Materials

Different samples of zirconium, titanium, and ceric arsenophosphates were prepared by varying the concentration and mixing ratios as mentioned in Table 1. The pH of the mixture was fixed in the pH range 0–1 by adding nitric acid or ammonium hydroxide as appropriate with constant stirring. The gels thus obtained were kept at room temperature (30 C) overnight and filtered, washed with DMW, and dried at 40 C in an air oven. The dried products were immersed in DMW and the granules were converted into the H^+ form as usual (5). On the basis of their stability and ion-exchange capacity, Samples S-3 and S-8 were selected for further studies. The reproducibility was checked by preparing the samples and observing their ion-exchange properties several times.

TABLE 1

Preparation of Zr(IV), Ti(IV), and Ce(IV) Arsenophosphates

Sample no	Sample	Concentration of mixing solutions (*M*)	Mixing ratio by volumes M.As.P	i.e.c (meq/dry g for Na^+)
S-1	Zirconium arsenophosphate	0.1	1:1:1	0.82
S-2	Zirconium arsenophosphate	0.1	1:2.1	0.84
S-3	Zirconium arsenophosphate	0.05	1:1:1	0.94
S-4	Titanium arsenophosphate	0.1	2.1:1	1.0
S-5	Titanium arsenophosphate	0.1	1:1:2	1.2
S-7	Titanium arsenophosphate	0.1	1:1:1	1.27
S-8	Titanium arsenophosphate	0.05	1.1:1	1.31
S-9	Ceric arsenophosphate	0.05	1.1:1	0.60

Composition

Zirconium Aresenophosphate. 500 mg of the powdered exchanger was fused with a mixture of powdered potassium carbonate (3 g) and powdered potassium nitrate (1 g) in a platinum crucible. After fusion the product was boiled with DMW, and the insoluble material was filtered and ignited to ZrO_2 (*8*) and weighed. The filtrate was analyzed for the arsenic and phosphorous content as before (*5*).

Titanium Arsenophosphate. 500 mg of the powdered exchanger was dissolved in 20 mL of 8 *M* H_2SO_4 by heating. Titanium was precipitated as its hydroxide by using NH_4OH, filtered, ignited to TiO_2 (*9*), and weighed. Arsenic and phosphorous were determined in the filtrate as above.

The Zr:As:P and Ti:As:P ratios in the two samples were found to be 2:1:1 and 3:1:1, respectively.

Ion-Exchange Capacity (i.e.c.)

The i.e.c. of Samples S-3 and S-8 was determined as usual by the column process (*5*). The values in meq/dry g for different metals were:

ZrAsP:Na(I)(0.94), K(I)(1.35), Mg(II)(0.83), Ca(II)(0.91)
TiAsP:Na(I)(1.31), K(I)(1.82), Mg(II)(1.17), Ca(II)(1.24)

Thermal Stability

The samples were heated at various temperatures in a muffle furnace for 1 h each and the i.e.c. was determined as usual after cooling them to room

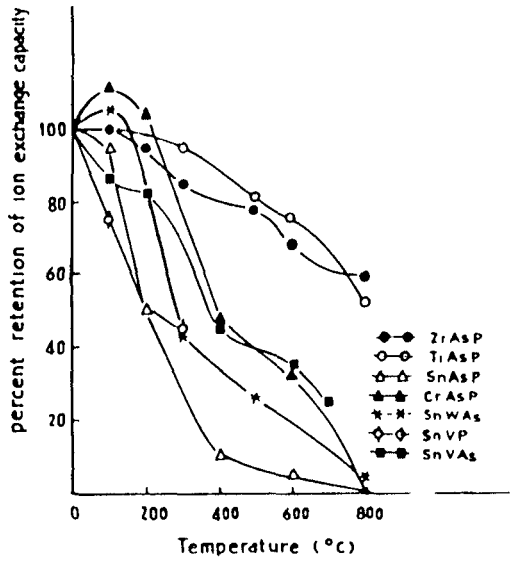


FIG. 1. Effect of temperature on the i e c of different double salts

temperature. Figure 1 shows the percent retention in the i.e.c. of some double salts such as Sn(IV) and Cr(III) arsenophosphates (*5*), Sn(IV) vandophosphate (*4*), Sn(IV) tungstoarsenate (*10*), and Sn(IV) vanadoarsenate (*11*), including those under study.

Chemical Stability

250 mg of the material was placed in a 25 mL solution of an acid or a base, with intermittent shaking for 24 h. The solution was then analyzed for the zirconium, titanium, phosphorous, and arsenic content by using standard spectrophotometric methods (*12–15*). Table 2 summarizes the results.

pH Titrations

500 mg of the exchanger was taken in each of several 250 mL conical flasks followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios (*16*), the final volume being 50 mL. The pH was recorded after keeping the solutions overnight for equilibrium and was plotted against the milliequivalents of OH added (Figs. 2 and 3).

TABLE 2

Chemical Stability of Zr(IV) and Ti(IV) Arsenophosphates

	Amount dissolved (mg)					
	Zr(IV) arsenophosphate			Ti(IV) arsenophosphate		
Solution	Zr	P	As	Ti	P	As
2 *M* HNO_3	0.06	0.13	0.20	10.5	0.9	0.84
4 *M* HNO_3	0.15	0.30	0.32	13.5	1.4	1.12
2 *M* HCl	0 06	0.38	0.42	7.2	1.75	1.60
4 *M* HCl	0.13	0.50	0.66	8.4	2.40	2.10
1 *M* H_2SO_4	0.56	0.45	0.60	11.2	2.70	2.50
2 *M* H_2SO_4	1.44	0.60	1.10	19.5	3.10	2.90
0.1 *M* KOH	0.12	6.80	7.10	0.0	5.30	4.40

Distribution Studies

These were performed in DMW and nitric acid (0.01 and 0.1 *M*) media for some common metal ions. 250 mg of the exchanger in the H^+ form was dipped in 25 mL of the solution containing the metal ion, not exceeding 3% of the total i.e.c. of the exchanger. The contents were shaken for 4 h at 30°C

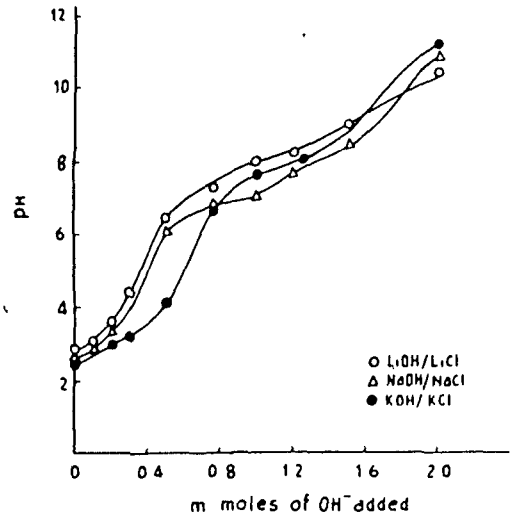


FIG. 2. pH titration curves for Zr(IV) arsenophosphate by added salt, batch method.

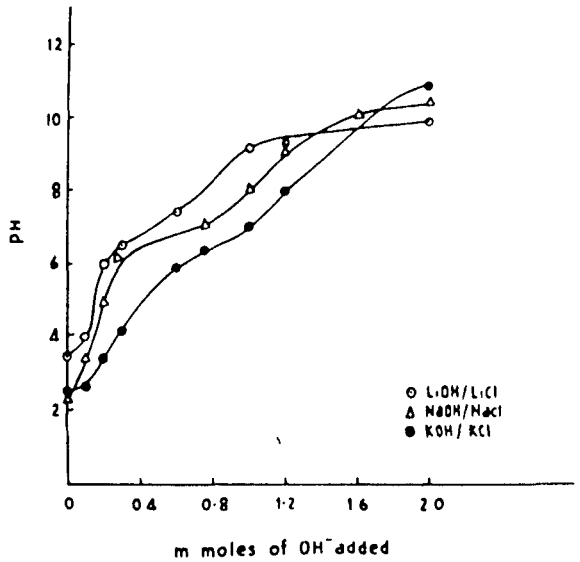


FIG. 3. pH titration curves for Ti(IV) arsenophosphate by added salt, batch method

to achieve equilibrium, and the metal ions left in the solution were determined with EDTA as usual (*17*) except for Ti(IV), UO_2(II), and Ce(IV) which were determined spectrophotometrically (*13*, *18*, *19*). The K_d values were calculated by the usual expression (*6*). The distribution coefficients (K_d in mL/g) are summarized in Table 3.

Separations Achieved

Several binary separations were tried using a column containing 2 g of the sized (35–100 mesh) exchanger particles taken in a glass tube having an i.d. of ~0.6 cm. The metal ions were eluted at a flow rate of ~0.5 mL/min using eluants selected on the basis of the K_d values obtained. The metal ions in the effluent were determined as described above, and the results are summarized in Table 4.

DISCUSSION

The two ion-exchange materials prepared in these studies show a high thermal stability. They possess an appreciable i.e.c. (0.6–0.7 meq/dry g) even after heating to 800°C, a peculiar and unusual characteristic of an inorganic ion exchanger. A comparison with similar salts (Fig. 1) indicates

TABLE 3

K_d Values of Metal Ions on Zr(IV) and Ti(IV) Arsenophosphates in Different Media[a]

	ZrAsP			TiAsP		
Metal ion	DMW	0.01 *M* HNO_3	0.1 *M* HNO_3	DMW	0.01 *M* HNO_3	0.1 *M* HNO_3
Mg(II)	134	0	0	48	0	0
Ca(II)	188	0	0	95	12	8
Ba(II)	390	46	32	1560	21	19
Sr(II)	170	0	0	6500	181	181
Zn(II)	255	11	0	227	35	0
Cd(II)	860	6	0	291	15	0
Hg(II)	800	4	0			
Pb(II)	TA	644	16	9500	1100	1100
Co(II)	360	40	1	—	—	—
Cu(II)	804	61	1	131	30	0
VO(II)	480	220	0	700	38	5
Ni(II)	217	10	9	48	0	0
Fe(III)	TA	TA	330	TA	2900	500
U(VI)	713	290	20	95	0	0
Y(III)	TA	2520	8	TA	160	4
Ce(III)	TA	124	35	TA	76	6
La(III)	TA	260	40	—	—	—
Al(III)	TA	860	0	TA	TA	0
Th(IV)	TA	460	89	TA	240	0
Ti(IV)	TA	TA	550	—	—	—
Ce(IV)	TA	525	440	550	525	400

[a]TA = total adsorption; (—) = metal ions not studied.

that the percent retention in the i.e.c. of zirconium and titanium arsenophosphates is higher than of any other compound of this type heated at temperatures ranging from 100 to 800°C. They can therefore be used for metal separations even after they have been heat treated. The solubilities of these materials in different acid and basic media indicate that they are fairly stable in 1 *M* mineral acids. Zirconium arsenophosphate appears to be more stable than the titanium salts in all the media used (Table 2). In alkali solutions above 0.1 *M*, both salts hydrolyze slowly. The elution of the H^+ ions from the column of the ion-exchange material depends on the concentration of the eluant used. When a fixed volume (120 mL) of $NaNO_3$ solutions of varying concentrations (0.1 to 1 *M*) was used as eluant, the maximum i.e.c. was observed at a concentration of 0.5 *M* and above. The nature of the elution curves was similar to the one obtained for Sn(IV) arsenophosphate (5).

TABLE 4

Binary Separations of Metal Ions Achieved on Zr(IV) and Ti(IV) Arsenophosphates

Sample no	Separation	Material used	Amount taken (μg)		Amount found (μg)		Error (%)		Eluant and its volume used for different metals
			M_1 (μg)	M_2 (μg)	M_1 (μg)	M_2 (μg)	M_1	M_2	
1	Mg–Sr	TiAsP	218 Mg	823 Sr	223 Mg	823 Sr	+2 3	0	Mg 0 001 *M* HNO_3, 60 mL Sr 0 1 *M* HNO_3, 60 mL
2	Mg–Ba	TiAsP	218 Mg	645 Ba	218 mg	631 Ba	0	−1 2	Mg 0 001 *M* HNO_3, 60 mL Ba 0 1 *M* HNO_3, 60 mL
3	Pb–Cu	TiAsP	597 Cu	1947 Pb	609 Cu	1906 Pb	+2 1	−2 2	Cu 0 1 *M* HNO_3, 50 mL Pb 1 *M* HNO_3 − 0 5 *M* NH_4NO_3, 60 mL
4	Pb–Hg	TiAsP	1925 Hg	1947 Pb	1925 Hg	1926 Pb	0	−1 1	Hg 0 1 *M* HNO_3 65 mL Pb 1 *M* HNO_3 − 0 5 *M* NH_4NO_3, 60 mL
5	Pb–Zn	TiAsP	313 Zn	1947 Pb	320 Zn	1947 Pb	+2 1	0	Zn 0 1 *M* HNO_3, 30 mL Pb 1 *M* HNO_3 − 0 5 *M* NH_4NO_3, 60 mL
6	Fe–Zn	ZrAsP	339 Zn	491 Fe	339 Zn	502 Fe	0	+1	Zn 0 1 *M* HNO_3, 40 mL Fe 2 *M* HNO_3, 80 mL
7	Fe–VO	ZrAsP	575 VO	491 Fe	586 VO	480 Fe	−1 2	−2 2	VO 0 1 *M* HNO_3, 40 mL Fe 2 *M* HNO_3, 85 mL
8	Fe–Cu	ZrAsP	584 Cu	491 Fe	584 Cu	491 Fe	0	0	Cu 0 1 *M* HNO_3, 30 mL Fe 2 *M* HNO_3, 80 mL
9	Ti–UO	ZrAsP	480 Ti	1270 UO	474 Ti	1280 UO	−1 2	−0 8	UO_2 0 1 *M* HNO_3, 40 mL Ti 0 2 *M* H_2SO_4 + 3% H_2O_2 40 mL
10	Ti–Ce	ZrAsP	480 Ti	1400 Ce	475 Ti	1390 Ce	−1 1	−0 8	Ce 0 5 *M* H_2SO_4 + 1 *M* $(NH_4)_2SO_4$ 50 mL Ti 0 2 *M* H_2SO_4 + 3% H_2O_2 40 mL

These ion exchangers are probably bifunctional in behavior as indicated by their pH-titration curves (Figs. 2 and 3). The curves also reveal that the materials have a higher affinity for K(I) than for Na(I) or Li(I), which may be due to a smaller hydrated radius of the K(I) ion (γ_hK(I) = 2.32 Å, γ_hNa(I) = 2.76 Å, γ_hLi(I) = 3.40 Å). The i.e.c. values observed in the column process also point to the same conclusion. In the KOH/KCl system the first inflection point is obtained at pH ~ 4.3 for ZrAsP and at pH ~ 5.3 for TiAsP. However, the second inflection is not very sharp, probably due to a slow ion-exchange process or a wide spread of effective pK_a values. The pH-titration curves indicate a higher i.e.c. than obtained in the column process. Less acidic protons might also be removed in the former case.

The IR spectra show a number of strong and sharp peaks at frequencies of ~800, ~1000, ~1400, ~1500, ~1600, and ~2900 cm^{-1}. The first peak is indicative of the M-O stretching vibrations (*20*), while the next three are due to the presence of HPO_4^{2-}, $HAsO_4^{2-}$, PO_4^{3-}, and AsO_4^{3-} in the structure. The presence of water of crystallization is shown by the peaks at ~1600 and ~2900 cm^{-1}. The peak at ~1600 cm^{-1} is also indicative of a strongly hydrogen bonded OH or an extremely strongly coordinated H_2O. On heating the exchanger up to 300°C, the peaks at ~1600 cm^{-1} are broadened and become less intensive, perhaps due to a decrease in the interstitial water molecules in the structure. The same peaks were also observed in the IR spectra of Sn(IV) and Cr(III) arsenophosphates (5).

On the basis of chemical composition, TGA (Fig. 4), and IR studies, the following tentative formula is proposed for these materials: $[(TiO_2)_3(H_3AsO_4)(H_3PO_4)]\cdot nH_2O$ and $[(ZrO_2)_2(H_3AsO_4)(H_3PO_4)]\cdot nH_2O$.

The value of n, the external water molecules, has been obtained using Alberti's equation (*21*).

$$18n = \frac{X(M + 18n)}{100}$$

where X = % weight loss in the material, M = molecular weight minus the external water molecules, and n = number of external water molecules.

From the TGA curves we find that the maximum weight loss is ~30% for both zirconium and titanium arsenophosphates. The weight loss observed at ~200°C is 12.5% for ZrAsP and 13% for TiAsP. If it is assumed that at this temperature only the external water molecules are removed from the exchanger, then the value of n, as obtained from the above equation, comes out to be ~4.

The potential of these ion exchangers has been demonstrated by achieving some important binary separations. For example, ZrAsP has shown the separation of Fe(III)–VO(II), Fe(III)–Cu(II), Fe(III)–Zn(II), Ti(IV)–

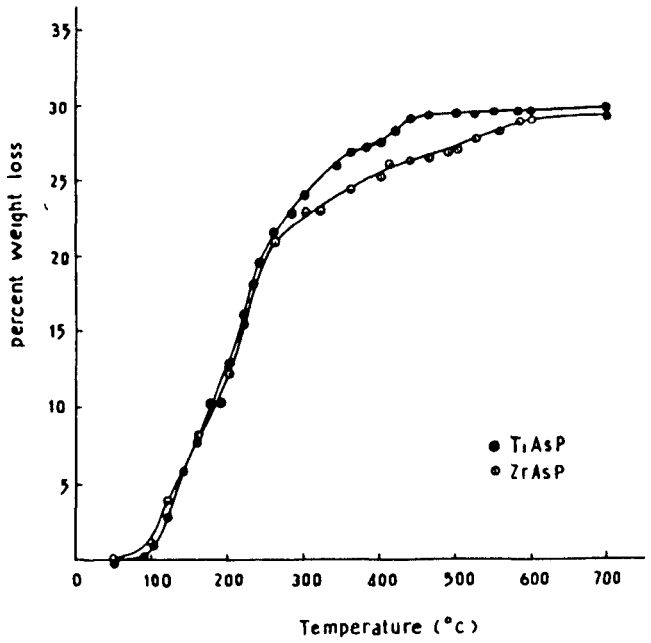


FIG. 4 TGA curves for Zr(IV) and Ti(IV) arsenophosphates in the H^+ form

UO_2(II), and Ti(IV)–Ce(IV) on its column, which are important from the industrial point of view. The exchanger may therefore be useful in the analysis of ferrous alloys. Similarly, TiAsP gives such separations as Pb(II)–Hg(II), Pb(II)–Cu(II), Pb(II)–Zn(II), Mg(II)–Sr(II), and Mg(II)–Ba(II) which are of analytical importance. It is also highly selective for Pb(II), indicating a possibility of adsorbing lead selectively from its alloy solutions. The elutions are quick and sharp, and the results are fairly precise and reproducible as summarized in Table 4.

Acknowledgements

The authors are thankful to Prof. M. Qureshi and Prof. W. Rahman for research facilities.

REFERENCES

1 C B Amphlett, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964
2 D Naumann, *Kernenergie*, 6, 173 (1963) (in German), *Chem Abstr*, *62*, 202b (1963)
3 S J Naqvi, D Huys, and L H Baetsle, *J Inorg Nucl Chem*, *33*, 4317 (1971)
4 M Qureshi and R C Kaushik, *Anal Chem*, *49*, 165 (1977)

5 K G Varshney and A A Khan, *J Inorg Nucl Chem*, *41*, 241 (1979)
6 K G Varshney and A A Khan, *Talanta*, *25*, 528 (1978)
7 K G Varshney, S Naheed, A A Khan, S N Tandon, and C B Gupta, *Chromatographia*, *12*, 473 (1979)
8 G Charlot and D Bezeir, *Quantitative Inorganic Analysis*, 3rd ed, Wiley, New York, 1957, p 638
9 Ref *8*, p 609
10 M Qureshi R Kumar, V Sharma, and I Khan, *J Chromatogr*, *118*, 175 (1976)
11 P S Thind S S Sandhu, and J P Rawat, *Chim Anal*, *24*, 65 (1979)
12 F D Snell and C T Snell *Colorimetric Methods of Analysis*, 3rd ed, Vol II, Van Nostrand Princeton, New Jersey, 1959, p 448
13 Ref *12* p 438
14 S R Olsen, C V Cole, F S Watanake, and L A Dean, *U S, Dep Agric, Circ 939*, 99 (1954)
15 E B Sandell, *Colorimetric Determination of Traces of Metals*, Vol 3, Interscience, New York 1959, p 282
16 N E Topp and K W Pepper *J Chem Soc*, p 3299 (1949)
17 C N Reilley, R W Schmid, and Fawzys, *J Chem Educ*, *36*, 555 (1959)
18 Ref *12*, p 492
19 Ref *12*, p 575
20 C N R Rao, *Chemical Application of Infra Red Spectroscopy*, Academic, New York, 1963, pp 338, 339, and 354
21 G Alberti E Torracca, and A Conte, *J Inorg Nucl Chem*, *28*, 607 (1966)

Received by editor January 20, 1981

SEPARATION SCIENCE AND TECHNOLOGY, 18(10), pp. 905-915, 1983

2.9 Ion-Exchange and Selectivity Behavior of Thermally Treated and γ-Irradiated Phases of Zirconium(IV) Arsenophosphate Cation Exchanger: Separation of Al(III) from Some Metal Ions and Removal of Cations from Water

K. G. VARSHNEY, KANAK VARSHNEY, and SANJAY AGRAWAL

CHEMISTRY SECTION
Z H COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH 202001, INDIA

Abstract

Ion-exchange and selectivity behavior of zirconium(IV) arsenophosphate (ZAP) has been studied systematically after thermal and irradiation treatments. As a result, an increase in the ion-exchange capacity and a complete reversal in the selectivity sequence for some common metal ions has been observed on heating. The modified phase of ZAP has been utilized successfully for the quantitative separation of aluminum from numerous metal ions and for the removal of cations from water.

INTRODUCTION

Zirconium(IV) arsenophosphate (ZAP), prepared earlier in these laboratories (*1*), has shown promising ion-exchange behavior for some common metal ions. It showed an increase in its ion-exchange capacity and an improvement in its chemical stability after thermal treatment. It was, therefore, decided to make a systematic study in this direction with the view of exploring the possibilities of some more useful applications of ZAP. The following pages summarize the ion-exchange behavior of the revised phases of this material after heat treatments and γ irradiation, and its application in separation science.

0149-6395/84/1810-0905$3.50/0

EXPERIMENTAL

Reagents

Zirconyl chloride, trisodium orthophosphate, and disodium arsenate used in this study were of AnalaR grade (98.5–99%) obtained either from the B.D.H. Poole (England) or from the E. Merck (Darmstadt).

Apparatus

pH measurements were made on an Elico (India) model LI-10 pH meter, and infrared studies were performed on a Beckman IR-20 spectrophotometer using KBr pellets. A Philips x-ray unit with a Mo-K_α target was used for x-ray studies, while a Bausch and Lomb spectronic-20 was used for colorimetry. Radiometric measurements were made in a well-type single channel analyzer with a NaI(Tl) detector obtained from the Electronic Corporation of India Ltd.

Synthesis of the Ion-Exchange Materials

ZAP was prepared (*1*) by the following method. Aqueous solutions (0.05 *M*) of zirconyl chloride, disodium arsenate, and trisodium orthophosphate were mixed in equal volumes and the pH of the mixture was fixed in the 0–1 range by adding nitric acid with constant stirring. The gel thus obtained was kept at room temperature (30°C) overnight and filtered, washed with demineralized water (DMW), and dried at 40 C in an air oven. The dried product was cracked in DMW to obtain granules which were converted into the H^+-form with 1 *M* HNO_3. It was then heated up to 200 and 400°C for 1 h each to get two separate phases, α-ZAP and β-ZAP, respectively, for further studies.

Ion-Exchange Capacity (i.e.c.)

The Na^+-ion exchange capacity of the material was determined by the column process (*1*). It was found to be 1.03 and 0.94 meq/dry g for α-ZAP and β-ZAP, respectively, with a coefficient of variation <0.5 for 10 observations. Figure 1 shows the percent retention of the i.e.c. on heating the material up to various temperatures.

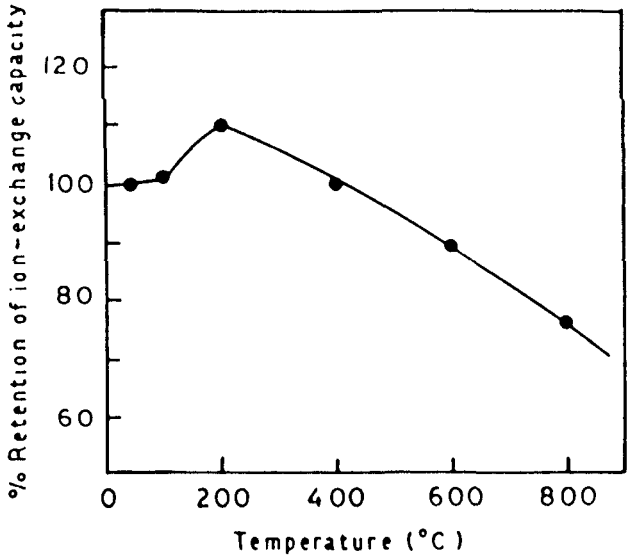


FIG. 1. Effect of temperature on the i.e.c. of Zr(IV) arsenophosphate.

γ-Irradiation

ZAP was exposed to γ-radiations obtained from a ^{60}Co-source for 96 h with a dose rate of 0.4 Mrd/h, $FeSO_4$ being the dosimeter. The sample thus obtained (γ-ZAP) showed an i.e.c. of 0.94 meq/dry g for Na^+.

Elution Behavior

250 mL $NaNO_3$ solutions of varying concentrations (0.1, 0.2, 0.5, and 1.0 *M*) were passed through several columns (internal diameter ~1 cm), each containing 1 g of α-ZAP in the H^+-form with a very slow flow rate (~0.5 mL/min). The H^+-ions thus eluted were titrated against a standard (0.1 *M*) NaOH solution and a maximum elution was observed with 1.0 *M* $NaNO_3$. To study the elution behavior, 100 mL of 1.0 *M* $NaNO_3$ solution was run through a column in the H^+-form and several 10 mL fractions of the effluent were collected at room temperature (30 ± 2°C). This was repeated at a working temperature of 95 ± 2°C by using a double-walled column, the outer part of which was surrounded by steam during the experiment. Figure 2

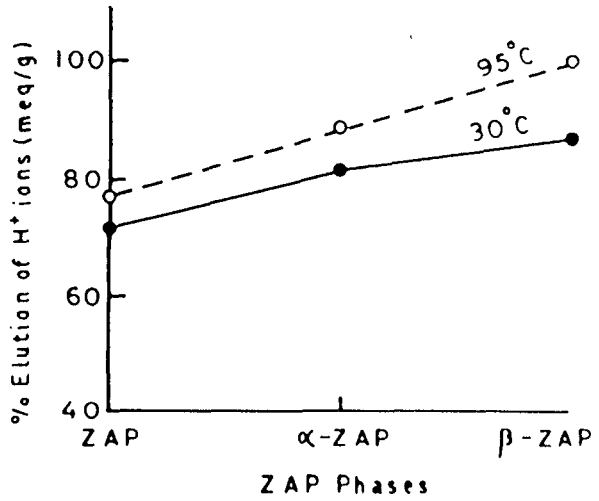


FIG. 2. Elution behavior of the various ZAP phases at 30 and 95 C as the working temperatures.

summarizes the percent elution of H^+-ions from the various phases studied, taking their original i.e.c. as the basis.

pH Titrations

pH titrations were performed by the method of Topp and Pepper (*2*) on the various phases. The curves are shown in Fig. 3.

Distribution Studies

250 mg of the sample was taken in a conical flask containing 25 mL of the solvent and shaken for 4 h at room temperature. Equilibrium was attained within 4 h as indicated by a concentration vs time curve. The metal ion concentration in the liquid phase was determined with EDTA (*3*). For alkali metals, however, the radiotracer technique was applied by taking the following isotopes (with their half-life periods shown in parentheses): ^{24}Na ·

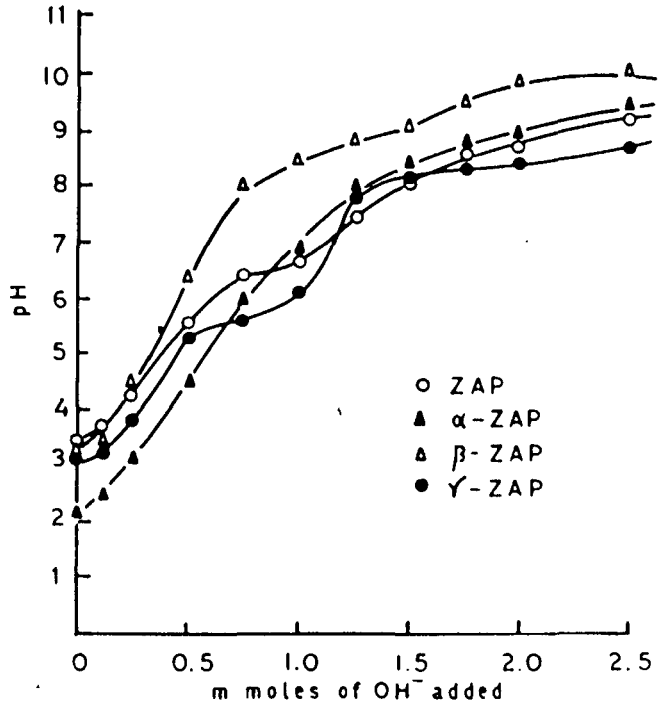


FIG. 3. pH titration curves for the various ZAP phases.

(15 h), ^{42}K (12.5 h), ^{86}Rb (18 days), ^{137}Cs (30.2 years). K_d values were calculated by

$$K_d = \left(\frac{1 - F}{F}\frac{V}{M}\right) \text{mL/g}$$

where F is the fraction of the total metal-ion concentration in the equilibrated solution phase, V is the volume of the solution (mL), and M is the mass of the exchanger (g). Table 1 summarizes the K_d values obtained on ZAP and α-ZAP samples in various solvents. Figure 4 shows the comparative distribution behavior of these two phases in DMW and 0.01 M HNO_3 solvent systems.

TABLE 1
K_d Values of Some Metal Ions on ZAP (*I*) and α-ZAP in Different Media

	$K_d \times 10^{-2}$									
	DMW		0.01 *M* HNO_3		0.10 *M* HNO_3		0.01 *M* $HClO_4$		0.10 *M* $HClO_4$	
Metal ion	ZAP	α-ZAP	ZAP	α-ZAP	ZAP	α-ZAP	ZAP	α-ZAP	ZAP	α-ZAP
Mg(II)	1.34	44.0	0.00	0.20	0.00	0.03	0.00	0.23	0.00	0.20
Al(III)	39.0	39.0	8.60	39.0	0.00	3.20	9.00	5.40	0.00	0.07
Ca(II)	1.88	37.0	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00
Mn(II)	5.25	35.3	0.36	0.52	0.00	0.45	0.20	0.16	0.00	0.06
Fe(III)	39.0	39.0	39.0	39.0	3.30	6.30	17.0	21.8	2.60	3.86
Co(II)	3.60	51.5	0.40	0.05	0.01	0.05	2.42	0.00	0.09	0.00
Ni(II)	2.17	51.5	0.10	0.68	0.09	0.20	0.12	0.05	0.08	0.00
Zn(II)	2.55	32.8	0.11	0.28	0.00	0.08	0.00	0.28	0.00	0.08
Sr(II)	1.70	31.5	0.00	0.00	0.00	0.00	0.12	1.40	0.00	0.97
Cd(II)	8.60	54.0	0.06	17.5	0.00	5.07	1.55	5.76	0.05	4.86
Ba(II)	3.90	19.0	0.46	0.83	0.32	0.65	0.58	1.31	0.36	1.06
Hg(II)	8.00	3.26	0.04	0 30	0.00	0.20	1.00	1.60	0.05	1 30
Pb(II)	56.5	56.5	6.44	3.60	0.16	2.68	5.66	2.68	0.18	0.67

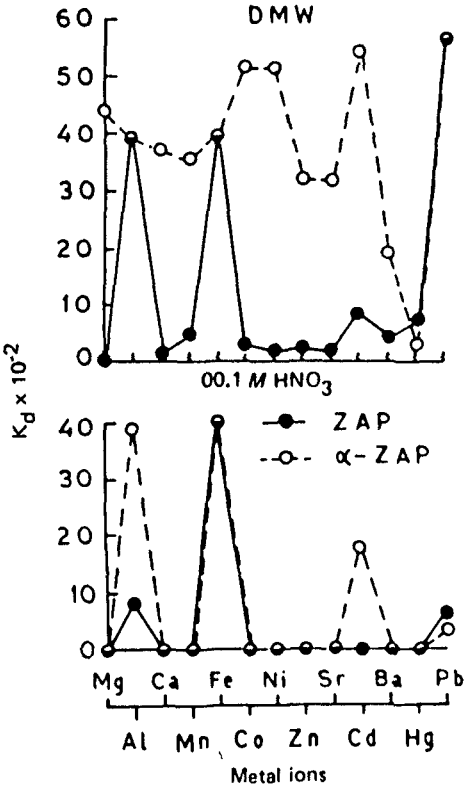


FIG. 4. Distribution behavior of ZAP and α-ZAP for various metal ions in DMW and 0.01 *M* HNO_3.

Separations Achieved

Two grams of the 60-100 mesh-sized particles of the exchanger (α-ZAP) in H^+-form were used for column operation in a glass tube having an internal diameter of ~0.6 cm. The column was then washed thoroughly with DMW and the mixture was loaded. After recycling 2 or 3 times to ensure complete adsorption of the mixture on the column bed, the elution of the metal ions other than Al(III) was done by 0.01 *M* HNO_3, selected on the basis of K_d values. Finally, aluminum(III) was removed with 0.1 *M* $HClO_4$. Table 2 summarizes the salient features of the separations achieved while Fig. 5 shows their elution curves.

TABLE 2
Some Salient Features of the Separations of Al(III) from Other Metal Ions on α ZAP Columns

No	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used and its volume (mL)	HETP (cm)
1	Mn(II)–Al(III)	137 5 Mn	141 4 Mn	2 8	0 01 *M* HNO_3, 50	0 375
		67 50 Al	67 50 Al	0 0	0 10 *M* $HClO_4$, 40	—
2	Mg(II)–Al(III)	60 00 Mg	60 00 Mg	0 0	0 01 *M* HNO_3, 40	0 135
		67 50 Al	67 50 Al	0 0	0 10 *M* $HClO_4$, 40	—
3	Ni(II)–Al(III)	146 8 Ni	139 8 Ni	−4 9	0 01 *M* HNO_3, 30	0 960
		67 50 Al	67 50 Al	0 0	0 10 *M* $HClO_4$, 50	—
4	Zn(II)–Al(III)	162 5 Zn	162 5 Zn	0 0	0 01 *M* HNO_3, 40	1 50
		67 50 Al	67 50 Al	0 0	0 10 *M* $HClO_4$, 40	—
5	Pb(II)–Al(III)	520 0 Pb	508 7 Pb	−2 2	0 01 *M* HNO_3, 50	1 50
		67 50 Al	65 39 Al	−3 1	0 10 *M* $HClO_4$, 40	—
6	Co(II)–Al(III)	147 3 Co	147 3 Co	0 0	0 01 *M* HNO_3, 50	0 735
		67 50 Al	67 50 Al	0 0	0 10 *M* $HClO_4$, 40	—
7	Al(III) from a synthetic mixture	137 5 Mn 60 00 Mg 146 8 Ni 162 5 Zn 520 0 Pb 147 3 Co	—	—	0 01 *M* HNO_3, 150	—
		67 50 Al	67 50 Al	0 0	0 10 *M* $HClO_4$, 40	—

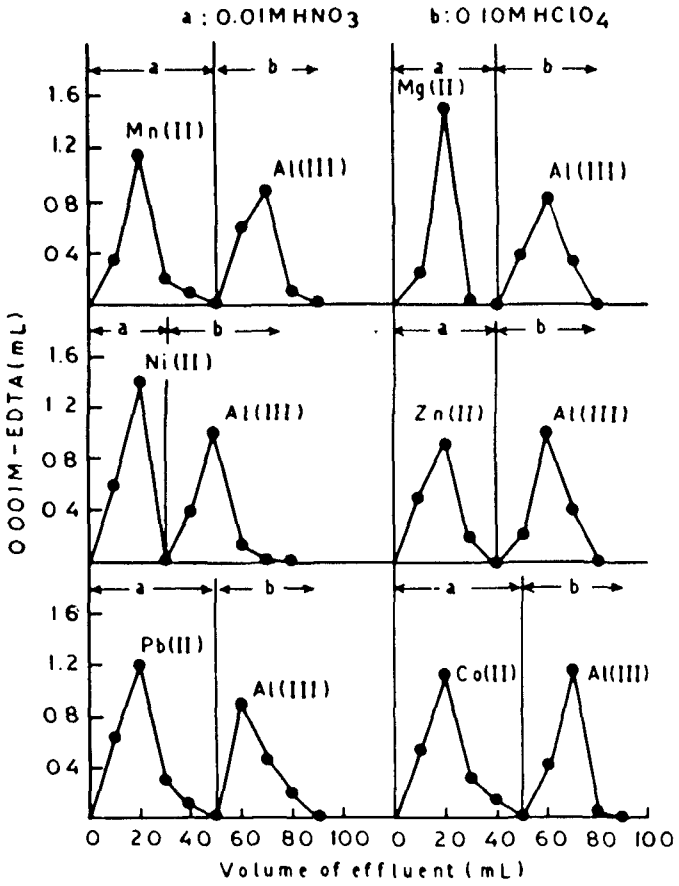


FIG. 5. Separation of Al(III) from other metal ions on α-ZAP columns.

DISCUSSION

This study highlights certain interesting features of zirconium(IV) arsenophosphate. As compared to the sample prepared after drying the gel at 40°C (ZAP), the sample obtained after heating it at 200°C for 1 h (α-ZAP) possesses a higher i.e.c. when determined at room temperature. Several repetitions invariably revealed that the increase in the i.e.c. is ~10% (Fig. 1). A higher working temperature (95 ± 2°C) further enhances this value. For example, the phase obtained after heating ZAP up to 400°C (β-ZAP) gives an i.e.c. almost equal to that of ZAP at room temperature. With 95°C as the working temperature, however, all three phases (ZAP, α-ZAP, and

β-ZAP) possess the same i.e.c. (1.2 meq/dry g). Thus a higher working temperature, preferably 95°C, appears to be more favorable for the exchange sites to become highly operative. A higher i.e.c. for α-ZAP as compared to ZAP is probably due to an irreversible removal of external water molecules on heating the material up to 200°C. This is substantiated by the thermogram of ZAP obtained in our earlier studies (*1*) which showed a weight loss equivalent to the net increase in the i.e.c. of ZAP on heating. The elution rate also appears to be affected by heating. It increases appreciably with an increase in the heating and working temperatures (Fig. 2). The pH-titration curve (Fig. 3) is, however, not affected significantly by the thermal treatment.

The effect of heating on the selectivity behavior of the material is summarized in Table 1. α-ZAP is highly selective for almost all the metal ions studied in DMW as against ZAP which is selective only for Al(III), Fe(III), Pb(II), and Cd(II) as Fig. 4 illustrates. In 0.01 *M* HNO_3, α-ZAP becomes selective only for Al(III), Fe(III), and Cd(II). These studies therefore reveal that α-ZAP has greater utility at elevated temperatures, which may be unsuitable for an ion-exchange resin. This material has also shown its potential for the quantitative separation of Al(III) from other metal ions, the results of which are shown in Table 2 and Fig. 5. The height equivalent to a theoretical plate (HETP) can be determined (*4*) by

$$\text{HETP} = \frac{Lb^2}{8V_{max}^2}$$

where L is the column height (12 cm), b is the peak width (mL) at a height of $0.368C_{max}$, and V_{max} is the eluant volume (mL) at peak. These values for the metals separated from Al(III) are summarized in Table 2.

Another important application of α-ZAP may be for the removal of metal ions from water. When a water sample containing metal impurities was passed through a small column (5 g) of α-ZAP, the impurities equivalent to 256 mg $CaCO_3$ were found removed from the sample. Since the ion exchanger is highly stable chemically, the effluant does not contain any amount of Zr(IV), P(V), or As(V) as determined by an atomic absorption spectrophotometer.

Table 3 summarizes the effect of γ irradiation on some of the physical and ion-exchange properties of ZAP. As is clear from this table, an irradiation up to $\sim 10^6$ rads has a negligible effect. Only the pH titration is slightly affected. It shows bifunctional behavior after being irradiated as against the normal monofunctional behavior of the material (Fig. 3).

IR studies of these new phases reveal the presence of the same functional groups as observed in ZAP prepared earlier (*1*). These observations

TABLE 3
Effect of Irradiation on Some Physical and Ion-Exchange Properties of ZAP

No	Ion-exchange property	Observations
1	Appearance	No change
2	Color	No change
3	Ion exchange capacity	No change
4	pH titration	Very slight change (Fig 3)
5	Elution behavior	Becomes slightly sharper on irradiation
6	Distribution behavior	Practically no change in the K_d values of alkali metals

supplement our experimental data about the persistance of i.e.c. in heated phases (α-ZAP and β-ZAP). X-ray diffractograms, however, do not show any peaks of appreciable intensity, thus indicating the amorphous nature of the material even on heating up to 400°C.

Acknowledgments

The authors thank Prof Mohsin Qureshi for research facilities and the CSIR (India) for financial assistance. Dr M. Sanker Das, Head, Analytical Chemistry Division, Bhabha Atomic Research Centre, Bombay, India, is thanked for the radiotracer facilities.

REFERENCES

1 K G Varshney and A Premadas, *Sep Sci Technol*, *16*, 793 (1981)
2 N E Topp and K W Pepper, *J Chem Soc*, p 3299 (1949)
3 C N Reilley, R W Schmid and Fawzys, *J Chem Educ*, *36*, 555 (1959)
4 P S Thind and H Singh, *J Indian Chem Soc*, 58, 1187 (1981)

Received by editor May 11, 1982
Revised May 27, 1983

Talanta Vol 30 No 12 pp 955-958 1983
Printed in Great Britain

0039 9140/83 $3 00 + 0 00
Pergamon Press Ltd

94

2.10 ANALYTICAL APPLICATIONS OF Zr(IV) AND Ti(IV) ARSENOPHOSPHATES AS ION-EXCHANGERS

K G VARSHNEY, S AGRAWAL, K VARSHNEY and A PRIMDAS*
Chemistry Section, Z H College of Engineering and Technology, Aligarh Muslim University, Aligarh-202001, India

M S RATHI and P P KHANNA
Wadia Institute of Himalayan Geology, Dehradun, India

(*Received* 26 *March* 1980 *Revised* 22 *March* 1983 *Accepted* 13 *May* 1983)

Summary—The distribution of 27 metal ions between zirconium and titanium arsenophosphate and demineralized water, perchloric acid and nitric acid has been studied On the basis of the results, several binary and ternary separations can be designed The data have been used in application of these materials to the analysis of certain alloys and rocks

Inorganic ion-exchangers have an advantage over their organic counterparts because of their higher stability They are also more selective For example, tin(IV) vanadophosphate,[1] vanadoarsenate[2] and tungstoarsenate[3] are selective for alkaline-earth metal ions Tin(IV) arsenophosphate[4] shows good affinity for some quadrivalent metal ions such as Th^{4+} and Zr^{4+} However, practically all the work published on these materials has been on their preparation and properties, and none on applications other than to simple binary or ternary mixtures The present work is aimed at remedying this situation, and illustrating the wider utility of these materials

Zirconium and titanium arsenophosphate, prepared by us earlier,[5] were selected for the study

EXPERIMENTAL

Reagents

Zirconyl chloride (J T Baker), titanium(IV) chloride (s g 1 73 BDH) trisodium orthophosphate (BDH), and disodium hydrogen arsenate (Merck) were used Other reagents and chemicals were of analytical grade

Synthesis of the ion exchange materials

Zirconium and titanium arsenophosphate (ZrAsP and TiAsP) were prepared as described earlier [5] It was observed that when the material was converted into the H^+-form by the usual batch (equilibrium) process and washed in a column with demineralized water (DMW) or dilute nitric acid the effluents were found (by atomic-absorption spectroscopy) to contain Al Mg Ca, Si, Fe and Mn These may have arisen from impurities present in the chemicals used for the synthesis Before use the exchangers were therefore thoroughly washed with 1 0 *M* nitric acid in a column until the effluent was free from the impurities mentioned The material thus obtained had improved reproducibility and enhanced ion exchange behaviour

Distribution studies

All the metal ion solutions used were prepared in DMW except those of the tervalent and quadrivalent ions, to which a few drops of the appropriate acid were added to prevent hydrolysis The distribution coefficients were determined[6] by equilibrating 250 mg of exchanger with 25 ml of solution containing an amount of metal ion equivalent to not more than 3% of the total ion-exchange capacity of the material and adjusted to the appropriate acidity *etc* Titanium, uranium and cerium were determined colorimetrically[7-9] and the other metal ions by FDTA titration,[10] before and after the equilibration The results obtained are summarized in Table 1

Separations

Synthetic mixtures A few synthetic binary and tertiary mixtures were prepared by mixing the metal ion solutions in the required volume ratios For column operation, the exchanger (60–100 mesh, 2 g, H^+-form) was used in a glass tube of ~0 6 cm bore A known volume (~0 5 ml) of sample solution was loaded on the column at a very slow flow-rate (~3 4 drops/min) and recycled through the column at least three times, with a 2–3 ml water wash between cycles, followed by elution with suitable solvents at a flow-rate of ~0 5 ml/min The effluent was monitored qualitatively by standard spot-tests[11] to determine the elution behaviour, and then separate samples were analysed quantitatively by the methods used for the distribution studies For brevity, the results, which were satisfactory are omitted Typical separations include V(IV) Fe(III) Ti(IV), Zn Pb Fe(III), Mn(II) Fe(III), Al Fe(III), Y Ti(IV) Ni Fe(III), Hg(II) Pb, Cd Pb, Y-Ce(IV), U(VI) Ce(IV), La Ce(IV), Ni Pb, V(IV) Pb

Alloy and rock samples Stock solutions of the alloys and rocks tested were prepared as follows The alloy (~30 mg accurately weighed) was dissolved in ~5 ml of *aqua regia* The solution was evaporated to ~1 ml and then diluted to volume in a 100-ml standard flask with DMW For the rock analysis, 100 mg of sample were fused with sodium hydroxide in a nickel crucible at dull red heat, followed by the leaching of the cooled melt with DMW and dilution to 1 litre (standard flask) with dilute hydrochloric acid

For the alloy analysis 1 ml of the stock solution was loaded on the column (2 g of exchanger) at a very slow rate as described above All the metal ions except iron(III) were eluted with 0 01 *M* nitric acid The iron(III) was then eluted with 0 1 *M* nitric acid Table 2 gives the results

For the rock analysis 0 5 or 1 ml of the stock solution was evaporated to dryness to remove the excess of acid The residue was taken up in DMW (~2 ml) and the solution was loaded on the exchanger (2 g) in the column, the rest of the

*Present address Chemical Laboratory, Atomic Minerals Div Department of Atomic Energy, Bangalore, India

Table 1. Distribution coefficients of some metal ions on ZrAsP and TiAsP

Metal ions	Distribution coefficients									
	DMW		0.01*M* $HClO_4$		0.1*M* $HClO_4$		0.01*M* HNO_3		0.1*M* HNO_3	
	ZrAsP	TiAsP	ZrAsP	TiAsP	ZrAsP	TiAsP	ZrAsP	TiAsP	ZrAsP	TiAsP
Mg(II)	134	48	0	0	0	0	0	0	0	0
Ca(II)	188	95	0	12	0	8	0	12	0	8
Cu(II)	804	131	25	4	0	0	61	30	1	0
Co(II)	360	122	242	82	9	25	40	40	1	0
Ni(II)	217	48	12	18	8	0	10	0	9	0
Zn(II)	255	227	0	0	0	0	11	35	0	0
Cd(II)	860	291	155	44	5	20	6	15	0	0
Hg(II)	800	18	100	5	5	0	4	8	0	0
Pb(II)	TA	9.5×10^3	566	567	18	233	644	1.1×10^3	16	1.1×10^3
Mn(II)	525	4	20	0	0	0	36	0	0	0
V(IV)	480	700	4	0	4	0	220	38	0	5
Fe(III)	TA	TA	1.7×10^3	20	260	0	TA	2.9×10^3	330	500
Al(III)	TA	TA	900	0	0	0	860	TA	0	0
Cr(III)	100	—	—	—	—	—	65	—	0	—
U(VI)	713	95	298	0	27	7	290	0	20	0
Y(III)	TA	TA	180	1	27	0	2.5×10^3	160	8	4
La(III)	TA	260	61	100	27	7	260	120	40	0
Tb(III)	TA	900	25	30	0	0	30	50	0	0
Ho(III)	TA	400	400	27	0	0	40	30	0	0
Gd(III)	TA	287	520	11	0	0	52	20	0	0
Nd(III)	TA	600	460	61	0	0	50	58	0	0
Pr(III)	260	576	80	59	35	0	88	71	0	0
Dy(III)	TA	230	1.0×10^3	10	3	0	110	20	3	0
Sm(III)	140	900	435	275	0	15	50	37	0	0
Th(IV)	TA	TA	1.2×10^3	37	232	63	460	240	89	0
Ce(IV)	TA	550	443	525	525	56	525	525	440	400
Ti(IV)	TA	—	TA	—	525	—	TA	—	550	—

TA = total adsorption; (–) = not studied.

Table 2 Quantitative separation of iron (with ZrAsP, from 1 ml of stock solution of iron base alloys)

	Composition of stock solution μg ml					Found μg	
Sample	Fe	Cr	Ni	Mn	Si	Eluent 0.01 M HNO_3 (100 ml)	Eluent 1 M HNO_3 (100 ml)
AISI-303	222.8	56.5	26.7	4.7	1.6	Cr 55.1 Ni 26.7 Mn 4.8 Si 1.7	Fe 22.5
AISI 347	219.4	56.5	31.4	4.7	1.6	Cr 55.5 Ni 31.4 Mn 4.8 Si 1.7	Fe 22.1

procedure being the same as for the alloys. All the metal ions except Al^{3+} and Fe^{3+} were eluted with DMW as usual. Al^{3+} was removed from the column with 0.1 *M* perchloric acid, and Fe^{3+} with 0.5 *M* hydrochloric acid/1 *M* ammonium chloride mixture. Table 3 summarizes the results.

Reproducibility of ion-exchange behaviour

Ten batches of ZrAsP were prepared and the ion-exchange capacity and K_d values determined as usual. The values were essentially the same in all cases.

DISCUSSION

The main purpose of this work was to study the distribution and separation of various metal ions on ZrAsP and TiAsP inorganic ion-exchangers. As the results show, the materials offer selectivity for a number of metal ions in various media. Though both exchangers generally show the same behaviour in some cases they differ remarkably. For example, Ti(IV) and Y(III) are found to be strongly sorbed by ZrAsP in 0.01 *M* nitric acid, but not by TiAsP, whereas Pb(II) is strongly sorbed by TiAsP in 0.1 *M* nitric acid, but not by ZrAsP.

The distribution studies indicate several possible separations, some of them useful for the analysis of alloys such as ferronickel and ferromanganese. Tantalum antimonate, reported earlier,[17] also gives some

Table 3 Quantitative separation of various constituents in rocks on ZrAsP

Rock sample	Volume of stock solution loaded, ml	Elements present μg						Elements eluted by eluent shown μg		
		Al	Fe	Si	Ca	Mg	Mn	DMW	0.1 M $HClO_4$ (50 ml)	0.5 M HCl + 1 M NH_4Cl (50 ml)
G-2	0.5	7.70	1.34	34.6	0.98	0.37	0.01	Si 32.6 Ca 1.12 Mg 0.34	Al 8.4	Fe 1.4
G-2	1.0	15.4	2.69	69.2	1.96	0.75	0.03	Si 73.3 Ca 1.96 Mg 0.68	Al 15.8	Fe 2.7
AGV-1	0.5	8.59	3.89	29.8	2.47	0.76	0.05	Si 30.1 Ca 2.5 Mg 0.76 Mn 0.04	Al 8.6	Fe 3.8
AGV-1	1.0	17.2	6.78	59.6	4.94	1.52	0.10	Si 51.7 Ca 4.9 Mg 1.53 Mn 0.06	Al 17.2	Fe 6.7
BHVO-1	0.5	6.85	6.00	2.45	7.70	3.60	0.08	Si 2.45 Ca 7.5 Mg 3.6 Mn 0.06	Al 6.9	Fe 6.9
BHVO-1	1.0	13.7	12.0	4.90	11.4	7.20	0.17	Si 5.1 Ca 11.3 Mg 7.2 Mn 0.14	Al 14.0	Fe 11.6
BCR-1	0.5	6.86	6.70	27.26	3.48	1.74	0.09	Si 27.0 Ca 3.4 Mg 1.8 Mn 0.08	Al 7.1	Fe 6.8
BCR-1	1.0	13.7	13.4	54.5	6.97	3.48	0.18	Si 53.9 Ca 6.7 Mg 3.3 Mn 0.13	Al 14.1	Fe 13.6
PCC-1	0.5	0.36	4.14	21.1	0.27	21.7	0.06	Si 22.3 Ca 0.29 Mg 21.8 Mn 0.05	Al 0.36	Fe 4.1
PCC-1	1.0	0.73	8.28	42.1	0.55	43.5	0.12	Si 43.3 Ca 0.57 Mg 42.0 Mn 0.09	Al 0.72	Fe 8.2

of these separations, but our methods cover a wider range of composition Titanium arsenate[13] and titanium phosphate[14] do not give these separations TiAsP is more selective than the simple titanium arsenate for lead

Because of its high affinity for iron and aluminium in certain media, ZrAsP has been tried for the analysis of alloys and rocks Table 2 gives the results for the quantitative separation of iron from two standard steel samples The error range was ~1% Analysis of rocks also gave satisfactory results (Table 3)

Acknowledgements—The authors are thankful to Professor M Qureshi for research facilities and to the CSIR (India) for financial assistance

REFERENCES

1 M Qureshi and R C Kaushik, *Anal Chem*, 1977, **49**, 165
2 P S Thind S S Sandhu and J P Rawat, *Chim Anal (Warsaw)*, 1979, **24**, 65
3 M Qureshi, R Kumar, V Sharma and T Khan, *J Chromatog*, 1976, **118**, 175
4 K G Varshney and A A Khan, *J Inorg Nucl Chem*, 1979, **41**, 241
5 K G Varshney and A Premadas, *Sepn Sci Technol*, 1981, **16**, 793
6 K G Varshney and A A Khan, *Talanta*, 1978, **25**, 528
7 F D Snell and C T Snell, *Colorimetric Methods of Analysis*, 3rd Ed, Vol II, p 438 Van Nostrand, Princeton, 1959
8 *Idem, op cit*, p 492
9 *Idem, op cit*, p 515
10 C N Reilley, R W Schmid and F S Sadek, *J Chem Educ*, 1959, **36**, 555
11 F Feigl and V Anger, *Spot Tests in Inorganic Analysis*, 6th Ed, Elsevier, Amsterdam, 1972
12 M Qureshi, J P Gupta and V Sharma, *Anal Chem*, 1973, **45**, 1901
13 M Qureshi and S A Nabi, *J Inorg Nucl Chem*, 1970, **32**, 2059
14 Y V Egorov, N V Dranitsina and N N Kagaker, *Tr Ural Politekh Inst*, 1970, **184**, 86

Indian Journal of Technology
Vol. 23, March 1985, pp. 114-115

2·11 Analytical Application of Zirconium(IV) Arsenophosphate in Analysis of Metals in Antacids

K G VARSHNEY, S AGRAWAL & K VARSHNEY
Analytical Laboratories, Chemistry Section,
Faculty of Engineering and Technology,
Aligarh Muslim University, Aligarh 202001, India

Received 27 *February* 1984; *accepted* 20 *December* 1984

The distribution coefficients of some metal ions have been determined on zirconium(IV) arsenophosphate cation exchanger. Based on this study, the separation of Al(III) from Mg(II) has been achieved in some synthetic mixtures and in marketed antacid formulations. The method is rapid, simple and selective with good accuracy and precision.

A wide variety of uses has been found for synthetic inorganic ion exchangers and new uses are constantly being suggested. The bulk of recent literature has dealt with their preparation, properties and application to simple binary or ternary separations of metal ions[1,2]. To illustrate their utility, we have earlier made an effort to analyze some standard rock and alloy samples using zirconium(IV) silico and phospho arsenate columns[3-5].

Ion-exchange technique has been useful in the assay of metallic species in drug formulations. Organic resins have been used by Korkisch and Huebner[6] to separate metallic species from various multivitamin preparations, prior to their determination by atomic absorption spectrophotometry. However, no attempt has so far been made in this direction using an inorganic ion exchanger. The present study was, therefore, carried out to explore the possibility of estimating aluminium and magnesium in some antacid formulations marketed under different trade names using zirconium(IV) arsenophosphate.

AnalaR grade zirconyl chloride, tri-sodium orthophosphate and di-sodium arsenate were obtained either from B.D.H. Poole (England) or E. Merck (Darmstadt).

Zirconium(IV) arsenophosphate (ZAP) was synthesized by the method reported earlier[7]. After converting into the H^+-form, it was thermally treated by keeping at various temperatures for 1 hr each in a muffle furnace. The Na^+-ion exchange capacities of various samples thus obtained are reported in Table 1. On this basis a heated phase of ZAP up to 200°C (ZAP-200) was selected for further studies.

The material was synthesized in ten batches following the same procedure and the ion-exchange capacities of the samples thus obtained were determined which were found to be the same in all cases. Ion-exchange capacities were also determined after several regeneration processes of the same sample. Up to five regenerations the ion-exchange capacity remains unchanged and on further use it decreases gradually.

The distribution coefficients (K_d) for various metal ions were determined as usual[7] by the batch process on ZAP-200. Table 2 shows these values in demineralized water (DMW) and HNO_3 media.

Analysis of the samples for aluminium and magnesium—Standard solutions containing different amounts of Al and Mg were prepared in DMW.

One tablet or 5 ml (for liquid preparations) of the antacid drug was treated with ~10 ml of conc. HCl and the clear solution thus obtained was diluted to 250 ml with DMW.

Table 1—Na^+ Exchange Capacity of ZAP after Thermal Treatment

Heating temperature, °C	Ion-exchange capacity meq/dry g	% Retention in ion-exchange capacity
45	0 94	100 0
100	0.95	101 1
200	1 03	109 6
400	0 94	100 0
600	0 84	89 4

Table 2—K_d Values of Various Metal Ions on ZAP-200

Metal ions	K_d			
	DMW	0 01 *M* HNO_3	0 1 *M* HNO_3	1 *M* HNO_3
Ba(II)	1900	83	65	0
Cd(II)	5400	1750	507	0
Pb(II)	5650	360	268	0
Mg(II)	4400	20	3	0
Sr(II)	3150	0	0	0
Hg(II)	326	30	20	0
Mn(II)	3530	52	45	0
Ca(II)	3700	0	0	0
Zn(II)	3280	28	8	0
Ni(II)	5150	68	20	0
Co(II)	5150	5	5	0
Cu(II)	3250	126	3	0
Sn(II)	1800	2	0	0
Fe(III)	3900	3900	630	0
Al(III)	3900	3900	320	0

Table 3 —Quantitative Separation of Aluminium and Magnesium From Some Indian Antacid Formulations on ZAP-200 Columns

Trade name of the antacid drug	Name of the drug manufacturing firm	Labelled composition[a], mg		Composition found by the proposed method[a], mg		% Deviation from the labelled composition		Coefficient of variance	
		$Al(OH)_3$	$Mg(OH)_2$	$Al(OH)_3$	$Mg(OH)_2$	$Al(OH)_3$	$Mg(OH)_2$	$Al(OH)_3$	$Mg(OH)_2$
Liquids:									
Alusil	Union Drug	300.0	250.0	297.63	251.42	−0.79	+0.57	1.53	0.68
Aludrox MH	Wyeth	305.0	100.0	301.05	98.15	−1.30	−1.85	1.08	0.48
Allugel DF	Unichem	200.0	200.0	198.40	194.80	−0.80	−2.60	1.53	1.17
Almagel	IDPL	125.0	125.0	123.16	125.33	−1.47	+0.26	1.53	0.83
Disilox	Stadmed	162.5	75.0	167.63	74.00	+3.16	−1.33	1.08	0.83
Diovol	Carter-Wallace	200.0	200.0	196.70	197.81	−1.65	−1.10	1.87	0.95
Gelusil	Warner	250.0	250.0	254.86	252.17	+1.94	+0.87	2.16	0.48
Gelumina MH	Cosma Farma	250.0	250.0	251.45	248.40	+0.58	−0.64	1.53	1.26
Mucaine	Wyeth	291.0	98.0	294.20	96.64	+1.10	−1.39	1.87	0.68
Logascid	Astra-IDL	200.0	200.0	201.84	203.85	+0.92	+1.93	1.53	1.07
Siloxogene	Searle	150.0	75.0	147.10	77.77	−1.93	+3.69	1.53	0.68
Tablets:									
Actigel	Thio-Pharma Falna	250.0	250.0	242.90	249.15	−2.84	−0.34	1.87	1.07
Siloxforte	Searle	300.0	150.0	292.50	155.53	−2.50	+3.69	2.42	0.68
Zymet	Parke Davis	250.0	250.0	248.02	256.70	−0.79	+2.68	2.42	1.39

[a]Per 5 ml/tablet of the drug.
[b]Each result is the mean of six replicates.

For the column operation, 2 g of ~60-100 mesh sized particles of the ion-exchange material (ZAP-200) in H^+-form were packed in a glass tube having an internal diameter ~ 0.6 cm and fitted with glass wool at the bottom. 1 ml of the analyte, which in the case of drugs was evaporated to almost dryness to remove the excess acid and the residue, taken in ~1 ml of DMW, was loaded on the column. The effluent was repassed through the column to assure complete adsorption of the ionic species. The Mg(II) and Al(III) ions were eluted with 0.01 *M* and 1 *M* HNO_3 solutions (max. volume ~ 100 ml) respectively, the rate of elution being ~3 ml/min, and were determined by the usual EDTA titrations. The analytical results are summarized in Tables 3 and 4.

It is clear from Table 1 that the material becomes more selective for the Na^+ ion when heated to 200°C, thus giving an enhanced ion-exchange capacity. The K_d values for various metal ions (Table 2) supplement this finding because as compared to the ordinary ZAP prepared earlier, the heated phase becomes more selective in aqueous medium for all the metal ions studied. This property of ZAP has been utilized for the quantitative separation of Al(III) from Mg(II). Tables 3 and 4 indicate the extent of accuracy and precision of the method for the analysis of synthetic mixtures and the real samples of antacid formulations, respectively. The proposed method is accurate, rapid and reproducible and a single ion-exchange column can be used several times as this material possesses a high regeneration power. It requires simple nitric acid as an eluant.

Table 4 —Quantitative Separation of Al(III) and Mg(II) in Their Synthetic Mixtures on ZAP-200 Columns

Amount loaded, μg		Amount found[a], μg		Error, %	
Al	Mg	Al	Mg	Al	Mg
67.5	60	67.50	60.06	0.00	+0.10
135	120	134.62	121.13	−0.28	+0.94
270	240	270.69	241.20	+0.26	+0.50
405	360	403.80	362.23	−0.30	+0.62
472.5	420	468.95	423.41	−0.75	+0.81

[a]Mean value of three replicates

We are grateful to the Council of Scientific and Industrial Research, New Delhi, for providing research fellowships to SA and KV.

References

1 *Ion exchange and solvent extraction*, edited by Marinsky J A & Marcus Y, Vol 5 (Marcel Dekker, New York) 1973, Ch 1.
2 Walton H F, *Anal Chem*, 52 (1980) 15R.
3 Varshney K G, Agrawal S & Varshney K, *Sep Sci Technol*, 18 (1983) 59.
4 Varshney K G, Agrawal S, Varshney K, Premadas A, Rathi M S & Khanna P P, *Talanta*, 30 (1983) 955.
5 Varshney K G, Agrawal S & Varshney K, *J Liq Chromatog*, 6 (1983) 1535.
6 Korkisch J & Huebner H, *Mikrochim Acta*, 2 (1976) 311.
7 Varshney K G & Premadas A, *Sep Sci Technol*, 16 (1981) 793.

ANALYTICAL LETTERS, 17(B18), 2111-2118 (1984)

12.12 QUANTITATIVE SEPARATION OF IRON FROM SOME MULTIVITAMIN-MULTIMINERAL FORMULATIONS USING ZIRCONIUM(IV) ARSENOPHOSPHATE COLUMNS

KEY WORDS: Iron, Separation, Multimineral Formulations, Zirconium(IV) Arsenophosphate, Inorganic Ion Exchanger

K.G.Varshney, Sanjay Agrawal, Kanak Varshney and Virendra Saxena

Analytical Laboratories
Chemistry Section
Z.H.College of Engineering and Technology
Aligarh Muslim University
Aligarh-202001 (India)

ABSTRACT

Iron has been separated quantitatively from various multivitamin-multimineral formulations on zirconium(IV) arsenophosphate columns. The method is simple and selective with a high degree of accuracy and precision.

INTRODUCTION

Determination of mineral elements in commercial pharmaceuticals has been a subject of several investigations using different analytical techniques[1-3]

 0003-2719/84/1718-2111$3.50/0

In most of the determination methods, severe interferences are caused due to presence of certain ions and separations are thus necessary prior to the determination. Korkisch et al. reported[9] that in the determination of metal ions in multivitamin preparations by atomic absorption spectrophotometry, iron interferes seriously which was separated on Dowex 1 x 8 anion exchange resin prior to the determination. The following pages summarize a method to separate iron from other metal ions in some multivitamin-multimineral formulations using zirconium(IV) arsenophosphate as a cation exchanger, in continuation of our efforts to explore the utility of such materials in the analysis of some real samples[10-13]

EXPERIMENTAL

Reagents and Chemicals

The zirconyl chloride and trisodium orthophosphate used in this study were the B.D.H. (England) products while disodium arsenate was an E.Merck (Darmstadt) product. Other reagents and chemicals were of analytical grade.

Preparation of the Ion-Exchange Material

Zirconium(IV) arsenophosphate as an amorphous material was prepared by our earlier method (14). It was heated at 200°C for 1 hour before using for

column operations as the phase obtained by this treatment is highly selective for iron.

Separations

Synthetic mixtures

Two grams of the 60-100 mesh sized particles of the exchanger (α-ZAP) in H^+-form were used for column operation in a glass tube having an internal diameter of ~0.6 cm. The column was washed thoroughly with demineralized water (DMW) and the mixture (1 ml) was loaded on it, maintaining a flow rate of ~0.1 ml/min. The elution of the metal ions other than Fe(II) was done by 0.01M HNO_3. Fe(II) was then eluted out with 4M HNO_3 with the simultaneous regeneration of the column. The rate of flow for the elution was kept ~1 ml/min. The metal ions in the effluents were determined quantitatively by EDTA titration except K(I), which was determined flame photometrically. The salient features of the separation of Fe(II) from other metal ions in some synthetic mixtures are summarized in Table 1.

Capsules and Tablets

One capsule/tablet was boiled with 5 ml of conc.HCl and 50 ml of DMW was added. After filtering through a Whatman No. 4 filter paper the solution was made upto 100 ml with DMW. One ml of this solution was evaporated to almost dryness and the residue was

TABLE 1

Some Salient Features of the Separation of Fe(III) From Other Metal Ions in Some Synthetic Mixtures

Separation achieved	Amount loaded, μg	Amount found,[a] μg	% Error	Eluent used	Volume of the eluent used, ml
Mg(II)-Fe(III)	120 Mg	119.61 Mg	-0.33 Mg	0.01N HNO_3	70
	280 Fe	282.55 Fe	+0.91 Fe	4N HNO_3	60
Ca(II)-Fe(II)	200 Ca	200.80 Ca	+0.40 Ca	0.01N HNO_3	50
	280 Fe	279.36 Fe	-0.23 Fe	4N HNO_3	60
Sr(II)-Fe(III)	327 Sr	328.10 Sr	+0.34 Sr	0.01N HNO_3	50
	280 Fe	279.36 Fe	-0.23 Fe	4N HNO_3	60
Na(II)-Fe(II)	575 Na	576.20 Na	+0.44 Na	0.01N HNO_3	80
	280 Fe	279.36 Fe	-0.23 Fe	4N HNO_3	60
Cu(II)-Fe(III)	318 Cu	321.26 Cu	+1.03 Cu	0.01N HNO_3	100
	280 Fe	278.73 Fe	-0.45 Fe	4N HNO_3	60
K(I)-Fe(II)	195 K	195.40 K	+0.21 K	0.01N HNO_3	50
	280 Fe	279.36 Fe	-0.23 Fe	4N HNO_3	60
Fe(III) from a multielemental synthetic mixture	120 Mg 200 Ca 327 Sr 575 Na 318 Cu 195 K	-	-	0.01N HNO_3	150
	280 Fe	278.10 Fe	-0.68 Fe	4N HNO_3	60

[a] Mean value of six replicates.

TABLE 2

Quantitative Separation of Fe(II) From Other Metal Ions in Various Multivitamin-Multimineral Formulations Marketed in India, on α -SAP Columns

Trade name of the drug and manufacturer	Labelled mineral composition (per capsule/tablet)	Composition determined* for iron	% Deviation from the labelled composition
Becadexamin (Glaxo)	Ferrous fumarate,50 mg; Calcium dibasic phosphate,70 mg; Copper sulphate,0.1 mg; Manganese sulphate,0.01 mg; Zinc sulphate,50 mg; Potassium iodide,0.025; Magnesium oxide,0.15 mg.	Ferrous fumarate 49.13 mg	-1.74
Multivite FM (Allenburys)	Ferrous fumarate,25 mg; Calcium dibasic phosphate,35 mg; Copper sulphate,0.1 mg; Manganese sulphate,0.01 mg; Zinc sulphate,50 mg; Potassium iodide, 0.025 mg; Magnesium oxide, 0.15 mg.	Ferrous fumarate 24.79 mg	-0.84
Compoferm (Bayers)	Dried ferrous sulfate,300 mg; Copper sulfate,0.2 mg; Manganese sulfate,1 mg.	Dried ferrous sulfate, 295.68 mg	-2.11
Nutrisan (Sandoz)	Ferrous fumarate,20 mg; Calcium gluconate,150 mg; Manganese chloride,0.5 mg; Zinc oxide,2 mg; Magnesium oxide, 1 mg.	Ferrous fumarate 19.79 mg	-1.05
Engren (Sarabhai)	Iron,10 mg; Calcium,0.15 mg; Copper,1 mg; Manganese,1 mg; Zinc,1.5 mg; Potassium,5 mg; Magnesium,6 mg.	Iron 10.04 mg	+0.40
Vitaminate Forte (Roche)	Dried ferrous sulphate,10.02 mg; Calcium phosphate,0.2 mg; Manganese hypophosphate,0.6 mg; Magnesium phosphate dibasic,44 mg.	Dried ferrous sulphate 10.06 mg	+0.38
Anemidox (Merck)	Ferrous fumarate,360 mg; Calcium carbonate,200 mg. 200 mg.	Ferrous fumarate 358.33 mg	-0.46
Gevral (Cyanamid)	Calcium pantothenate,5 mg; Ferrous fumarate,30 mg; Potassium iodide,0.1 mg; Calcium dibasic phosphate,500 mg; Cupric oxide,1.25 mg; Manganese dioxide,1.54 mg; Magnesium oxide,1.65 mg; Potassium sulphate,11.2 mg; Zinc oxide,0.62 mg.	Ferrous fumarate 30.21 mg	+0.70

*Mean value of six replicates.

taken in ~1 ml of DMF. It was then loaded on the column of the ion exchanger by the same procedure as described for the synthetic mixtures. All the metal ions except iron were eluted out with 0.01M HNO_3 (max.vol.required ~150 ml). Iron was finally removed with 4M HNO_3 (max.vol.required ~50 ml) and determined quantitatively by EDTA titration at pH 4 and using Cu-PAN indicator. The results are summarized in Table 2.

RESULTS AND DISCUSSION

The main feature of these studies is the separation of iron from other minerals in some multivitamin-multimineral formulations on zirconium(IV) arsenophosphate columns. The method is applicable to the synthetic mixtures (Table 1) as well as to the drug samples (Table 2) and is based on the high selectivity of the ion exchanger for iron. It shows a high degree of accuracy and precision with a coefficient of variance < 2. Thus, an amorphous phase of zirconium(IV) arsenophosphate has a great potential for its use in the analysis of pharmaceutical products.

ACKNOWLEDGEMENTS

Authors are grateful to Prof.M.Qureshi for the research facilities and to the Council of Scientific

& Industrial Research, India for the financial assistance.

REFERENCES

1. M.E.A.Cooper, J.Ballantine and A.D.Woolfson, J.Pharm.Pharmacol., 31, 403 (1979).
2. B.Stankovic, M.Dugandzic and M.Jelikic, Pharmazie, 32, 414 (1977).
3. Daniel J.J.Sullivan, Assoc.Off.Anal.Chem., 59, 1156 (1976).
4. Daniel J.J.Sullivan, Assoc.Off.Anal.Chem., 60, 1350 (1977).
5. S.W.Bishara and F.M.El-Samman, Microchem.J., 22, 442 (1977).
6. F.Pellerin and J.P.Goulle, Ann.Pharm.Fr., 35, 189 (1977).
7. Pentti O.Kosonen, Anne-Marie Salonen and Anna-Liisa Niewminen, Finn.Chem.Lett., 4, 135 (1978).
8. S.A.El-Kinawy, M.I.Walash, M.S.Abou-Bakr and I.Z.Diale, J.Drug Res., 7, 151 (1975).
9. J.Korkisch and H.Huebner, Mikrochim.Acta, 2, 311 (1976).
10. K.G.Varshney, S.Agrawal and K.Varshney, Sep.Sci. Technol., 18, 59 (1983).
11. K.G.Varshney, S.Agrawal, K.Varshney, A.Premadis, M.S.Rathi and P.P.Khanna, Talanta, 30, 935 (1983).

12. K.G.Varshney, S.Agrawal and K.Varshney, J.Liq. Chromotog., 6, 1535 (1983).

13. K.G.Varshney, S.Agrawal and K.Varshney, Anal. Lett., 16, 685 (1983).

14. K.G.Varshney, K.Varshney and S.Agrawal, Sep.Sci. Technol., 18, 905 (1983).

Received July 20, 1984
Accepted September 18, 1984

Talanta Vol 25 pp 528–530
© Pergamon Press Ltd 1978 Printed in Great Britain
0039-9140/78/0901-0528 $02.00/0

108

2-13 STABILITY AND DISTRIBUTION STUDIES ON Sn(IV) AND Cr(III) ARSENOPHOSPHATES· SEPARATIONS OF METAL IONS

K G VARSHNEY and ASIF A KHAN

Chemistry Section, Z H College of Engineering and Technology, A M U Aligarh (U P), 202001 India

(*Received* 19 *December* 1977 *Accepted* 14 *March* 1978)

Summary The stability of tin(IV) and chromium(III) arsenophosphates in mineral acids and sodium hydroxide has been investigated Structures for the two compounds are proposed based on the results of thermogravimetric analysis. K_d values for metal ions on these two compounds have been determined and separations of UO_2^{2+} Th^{4+}, UO_2^{2+} Zr^{4+} and Na^+ K^+ achieved

The inorganic ion-exchange materials produced by mixing a solution containing two anionic species with a metal ion solution have shown better ion-exchange properties than the zirconium phosphate type materials [1] In an earlier publication[2] we reported the preparation of tin(IV) and chromium(III) arsenophosphates Their composition, ion-exchange capacity, concentration and elution curves, thermal stability and pH titrations have been studied in detail Infrared and X-ray studies have also been made on these ion-exchange materials The present paper summarizes the chemical stability of these materials and the distribution behaviour of metal ions on them

EXPERIMENTAL

Preparation of ion-exchange materials

Tin(IV) arsenophosphate was prepared by mixing equal volumes of 0·1*M* solutions of tin(IV) chloride, sodium arsenate and sodium phosphate The pH of the mixture was adjusted to 0·0 with nitric acid The gel thus prepared was kept at room temperature for 24 hr and filtered off It was washed several times with distilled water and dried at 40 The dried material was crushed and converted into the hydrogen form with 1*M* nitric acid The material was finally washed with demineralized water to remove the excess of acid, and dried at 40 Granules of the required size were obtained by sieving The chromium(III) arsenophosphate was prepared by mixing 0·1*M* solutions of chromium(III) nitrate sodium arsenate and sodium phosphate in 2 1 1 volume ratio and treating the precipitate as described above The ion-exchange capacities of the two arsenophosphates for sodium ions were 1·75 and 0·74 meq g respectively, as reported earlier [2]

Chemical stability

Portions of ion-exchange material (500 mg) were placed in 25 ml of various mineral acids and sodium hydroxide solutions (of various concentrations) for 24 hr, with intermittent shaking The supernatant liquid was then decanted and analysed for Sn(IV), Cr(III), As(V) and PO_4^{3-} by standard spectrophotometric methods [3–6] The results are summarized in Table 1 The results of a thermogravimetric study of the two arsenophosphates are given in Fig 1

Distribution studies

Distribution studies of 16 metal ions on the two arsenophosphates were performed at pH 2 (adjusted with perchloric acid) The results are summarized in Table 2

Distribution coefficients (K_d) *of* Na^+, K^+, UO_2^{2+}, Th^{4+} *and* Zr^{4+} Sodium nitrate and potassium nitrate solutions were prepared in demineralized water The amount of the metal solution loaded was so adjusted that it did not exceed 3% of the total ion-exchange capacity of the exchanger Equilibrium was attained by keeping the solution overnight at room temperature in contact with the ion-exchange material The

Table 1(*a*) Chemical stability of Sn(IV) arsenophosphate

Solution	Sn(IV) dissolved, *mg*	As dissolved, *mg*	PO_4^{3-} dissolved *mg*
5*M* HCl	0·7$_5$	0·1$_5$	0·4
7*M* HCl	1·2$_5$	1·8·0	3·6·0
10*M* HCl	dissolved completely		
5*M* HNO_3	—	0·1	0·2
7*M* HNO_3	0·4	0·6	0·8
10*M* HNO_3	1·1	3·7$_5$	9·0
13*M* HNO_3	1·5	10·4	13·5
16*M* HNO_3	4·0	30·0	54·8
7*M* H_2SO_4	0·4	0·3	0·4
10*M* H_2SO_4	1·5	3·0	4·0
15*M* H_2SO_4	4·2	7·0	8·1
20*M* H_2SO_4	6·0	9·0	18·0
25*M* H_2SO_4	8·0	24·0	54·8
30*M* H_2SO_4	—	dissolved completely	
0·1*M* NaOH	1·5	3·0	6·7
0·5*M* NaOH	3·6	4·4	27·4
1·0*M* NaOH	8·0	30·0	57·3

Table 1(*b*) Chemical stability of Cr(III) arsenophosphate

Solution	Cr(III) dissolved *mg*	As(V) dissolved *mg*	PO_4^{3-} dissolved, *mg*
2·5*M* HCl	0·1	0·1$_5$	0·3
3*M* HCl	0·1	0·2	0·5
5*M* HCl	3·0	3·0	7·7
7*M* HCl	dissolved appreciably		
10*M* HCl	dissolved completely		
3*M* HNO_3	0·1$_5$	0·2	0·5
5*M* HNO_3	1·1$_5$	1·5	4·0
7*M* HNO_3	7·0	7·4	18·0
10*M* HNO_3	11·7	10·6	27·0
13*M* HNO_3	dissolved appreciably		
16*M* HNO_3	dissolved completely		
2*M* H_2SO_4	0·0$_5$	0·1	
3*M* H_2SO_4	0·2	0·3	0·5
5*M* H_2SO_4	0·4	0·6	1·8
7*M* H_2SO_4	1·4	2·2	4·7
10*M* H_2SO_4	6·0	6·0	13·5
15*M* H_2SO_4	8·2	9·0	16·0
20*M* H_2SO_4	18·4	20·4	51·0
25*M* H_2SO_4	dissolved appreciably		
0·01*M* NaOH		1·1	
0·1*M* NaOH	1·0	3·0	5·3
0·5*M* NaOH	14·0	21·0	12·0
1*M* NaOH	dissolved appreciably		

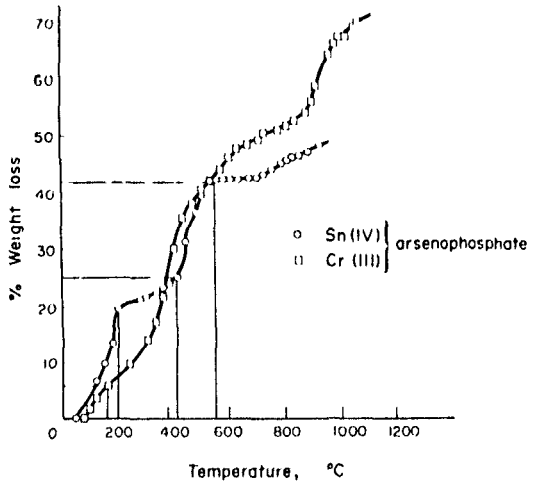


Fig 1 TGA curves for Sn(IV) and Cr(III) arsenophosphates in the H^+ form

Table 2 K_d values of metal ions on Sn(IV) and Cr(III) arsenophosphates at pH 2

Metal ion	K_d values, ml/g*	
	on Sn(IV) arsenophosphate	on Cr(III) arsenophosphate
Na^+	385 0	298 0
K^+	C A	C A
UO_2^{2+}	7 1	C A
Zr^{4+}	C A	C A
Th^{4+}	C A	C A
Ag^+	87 4	99 2
Hg^{2+}	2 3	6 2
Zn^{2+}	351 0	19 6
Rb^+	267 0	31 8
Cs^+	119 0	8 6
Sr^{2+}	16 0	0 3
Co^{2+}	47 8	2 4
Mn^{2+}	78 5	12 1
In^{3+}	30 2	94 2
Y^{3+}	288 0	6 4
Tb^{3+}	20 0	0 2

*C.A. = Complete adsorption.

Table 3 K_d values of Na^+ and K^+ in water and mineral acids

Solvent	K_d values, ml/g*			
	On Sn(IV) arsenophosphate		On Cr(III) arsenophosphate	
	Na^+	K^+	Na^+	K^+
Water	$8\,65 \times 10^3$	C A	$2\,85 \times 10^3$	C A
0 01*M* HCl	523 0	C A	65 0	C A
0 1*M* HCl	234 0	$8\,65 \times 10^3$	57 4	C A
1 0*M* HCl	85 9	312 0	37 0	C A
0 01*M* H_2SO_4	240 0	C A	$2\,12 \times 10^3$	C A
0 1*M* H_2SO_4	298 0	C A	$1\,04 \times 10^3$	C A
1 0*M* H_2SO_4	185 0	$8\,65 \times 10^3$	79 8	C A
0 01*M* HNO_3	240 0	C A	$1\,68 \times 10^3$	C A
0 1*M* HNO_3	186 0	$8\,65 \times 10^3$	619 0	C A
1 0*M* HNO_3	85 9	C A	571 0	C A

*C A = Complete adsorption

amounts of Na^+ and K^+ in the solution before and after equilibrium were determined by flame photometry Determinations were also made in hydrochloric, sulphuric and nitric acids (Table 3)

The K_d values of UO_2^{2+} were determined spectrophotometrically with hydrogen peroxide as the colorimetric reagent [7] Th^{4+} and Zr^{4+} were determined by EDTA titration

Distribution coefficients of Ag^+, Hg^{2+}, Zn^{2+}, Rb^+, Ca^{2+}, Sr^{2+}, Co^{2+}, Mn^{2+}, In^{3+}, Y^{3+} and Tb^{3+} The K_d values of these metal ions were obtained by using radioactive tracers The solutions were prepared in demineralized water and the pH was adjusted to 2 with perchloric acid The amount of exchanger taken was 100 mg and 10 ml of 10^{-3} *M* solution were loaded on the material The equilibrium was attained by keeping the material in the solution overnight at room temperature with occasional shaking The activity of the solution was measured with a G M counter or a scintillation counter

The formula used for the calculation of K_d values was

$$K_d = \frac{I - F}{F} \times \frac{V}{W} \text{ (ml g)}$$

where I is the initial concentration of the ion in solution F is the final concentration of the ion in solution V is the volume of solution and W the weight of the ion exchanger

Separations achieved

The columns were prepared from 0 5 g of the material (200–400 mesh) in a microburette The metal solutions were then loaded separately and eluted with suitable solvent The elution curves were obtained by plotting the weight of metal in the eluate against volume On the basis of the elution curves separations of UO_2^{2+}–Zr^{4+}, UO_2^{2+}–Th^{4+} and Na^+–K^+ were attempted Uranium was completely eluted with demineralized water, and zirconium and thorium were eluted with 1 *M* nitric acid For separating Na^+ from K^+, different concentrations of perchloric acid were used Na^+ was first eluted with 10^{-3} *M* perchloric acid and K^+ with 0 1*M* perchloric acid Figures 2 and 3 summarize these separations

DISCUSSION

It is clear from Table 1 that the materials obtained by mixing arsenates and phosphates with Sn(IV) and Cr(III) are acid-resistant Hydrochloric sulphuric and nitric acids at concentrations up to 4 *M* have no effect even after 24 hr contact at room temperature Higher concentrations have an appreciable effect nitric acid being the least and hydrochloric acid the most effective solvent Sodium hydroxide also dissolves the samples forming arsenate and phosphate In this respect these materials are superior to the analogous single salts such as chromium(III) phosphate [8] tin(IV) phosphate [9] chromium(III) arsenate [10,11] and tin(IV) arsenate [12]

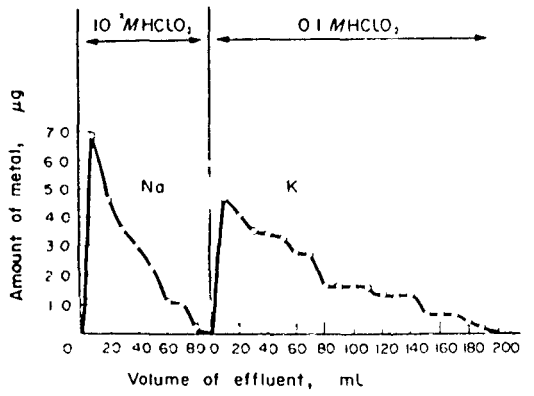


Fig 2(a) Separation of sodium from potassium on Sn(IV) arsenophosphate

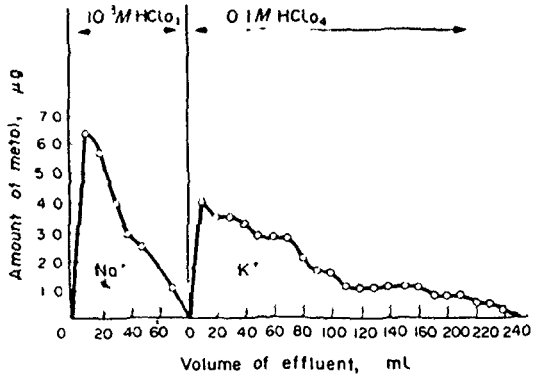
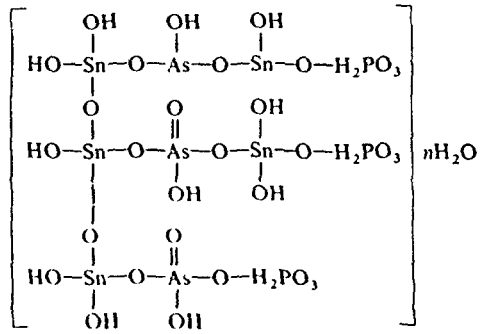


Fig 2(b) Separation of sodium from potassium on Cr(III) arsenophosphate

Earlier studies[2] gave the ratio of Sn(IV), As and P as 5.3·3 in tin(IV) arsenophosphate The following formula for this compound can, therefore be tentatively suggested,

$$[(SnO_2)_5\ (H_3AsO_4)_3\ (H_3PO_4)_3]nH_2O$$

and its structure written as



The number of external water molecules (n) can be estimated from the thermogravimetric study From Fig 1 it can be seen that tin(IV) arsenophosphate experiences a weight loss of 20% up to a temperature of 200° If it is assumed that all the external water molecules are removed on heating to this temperature then

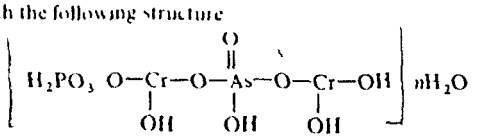
$$18n = \frac{x(M + 18n)}{100}$$

where x is % weight loss at 200 $M + 18n$ is the molecular weight of the material and n the number of external water molecules This gives the value of n as ~20

Similarly the formula for chromium(III) arsenophosphate, based on its composition [2] can be written as

$$[Cr_2O_3\ H_3AsO_4\ H_3PO_4]nH_2O$$

with the following structure



The number of external water molecules is found to be ~2

The thermogravimetric curves for these two salts in the H^+ form have some interesting features The total weight loss is much higher for chromium(III) arsenophosphate than for tin(IV) arsenophosphate The condensation of the molecule of the tin(IV) salt starts above 400 and is complete at 550 Chromium(III) arsenophosphate, on the other hand, continues to lose weight up to a temperature of 1100

Distribution studies of metal ions on these ion-exchange materials were made at pH 2 It was observed that these

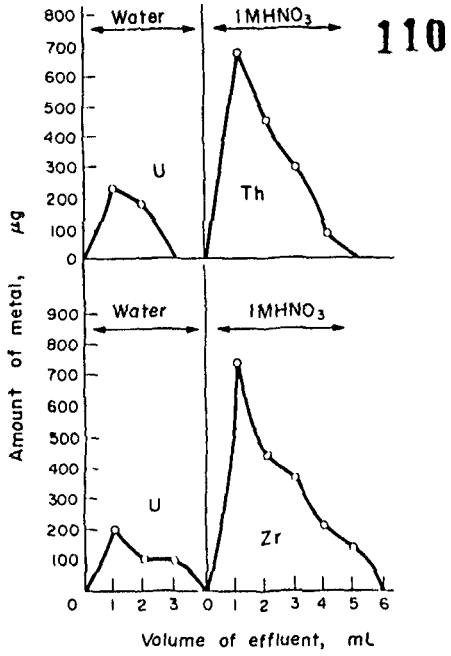


Fig 3 Separation of uranium from zirconium and thorium from uranium on Sn(IV) arsenophosphate

arsenophosphates are highly selective for K^+, Zr^{4+} and Th^{4+} The behaviour of UO_2^{2+} is unusual, however, its adsorption being negligible on tin(IV) arsenophosphate but complete on the chromium(III) salt UO_2^{2+} has therefore been separated from Zr^{4+} or Th^{4+} on tin(IV) arsenophosphate (Fig 3) Na^+ has been separated from K^+ on both materials since they have a very wide difference in their selectivities for these two ions As shown in Table 3 the K_d values of Na^+ and K^+ were also determined in water and in different concentrations of hydrochloric, sulphuric and nitric acids on both ion-exchangers It is interesting to note that K^+ is completely adsorbed on chromium(III) arsenophosphate in all solvent systems On the tin(IV) salt also, this metal ion tends to be strongly adsorbed except in 1·0M hydrochloric acid, in which it has a low K_d value

Acknowledgement The authors are thankful to Professor Mohsin Qureshi for research facilities Dr S N Tandon, Chemistry Department, University of Roorkee, Roorkee, India is thanked for the radioactivity facilities

REFERENCES

1. V Pekárek and V Vesely, *Talanta*, 1972, **19**, 1245
2. K G Varshney and A A Khan, *J Inorg Nucl Chem*, in the press
3. E B Sandell, *Colorimetric Determination of Traces of Metals* 3rd Ed, p 864 Interscience, New York, 1959
4. *Idem, ibid*, p 396
5. *Idem, ibid*, p 282
6. S R Olsen, C V Cole, F S Watanake and L A. Dean, *U S Dept Agric Circ*, No 939, 1954, 99
7. E B Sandell, *Colorimetric Determinations of Traces of Metals*, 3rd Ed, p 916 Interscience, New York, 1959
8. D Betteridge and G W Stradling, *J Inorg Nucl Chem*, 1967, **24**, 2652
9. Y Inoue, *ibid*, 1969, **26**, 2241
10. G M Lukaszewski and J P Redfern, *J Chem Soc*, 1962 4802
11. G M Lukaszewski J P Redfern and J E Salmon, *ibid*, 1961, 39
12. M Qureshi, H S Rathore and R Kumar, *ibid*, 1970, 1986

Annali di Chimica 1981 by Societa Chimica Italiana

2.14 pH-TITRATION AND DISTRIBUTION STUDIES OF ALKALI METAL IONS ON AMORPHOUS Sn(IV) AND Cr(III) ARSENATEPHOSPHATES: SEPARATION OF METAL IONS

Krishna Gopal VARSHNEY, Asif Ali KHAN and PREMADAS

Chemistry Section, Z.H. College of Engineering and Technology, Aligarh Muslim University, ALIGARH-202001 (INDIA).

Summary - The ion-exchange behaviour of Sn(IV) and Cr(III) arsenatephosphates has been examined for the systems Li(I)/H(I), Na(I)/H(I), K(I)/H(I) and NH_4(I)/H(I) using nonequilibrium pH-titrations. Distribution coefficients for Na(I) and K(I) in different concentrations of mineral acids have also been determined on these ion-exchange materials and chromium arsenatephosphate has been found to show high selectivity for potassium ion even under strongly acidic conditions. Quantitative separations of metal ions from some ternary and binary mixtures have been achieved on columns based on their distribution studies.

Riassunto - Il comportamento di arsenofostati di Sn(IV) e Cr(III) come scambiatori di ioni è stato esaminato per i sistemi Li(I)/H(I), Na(I)/H(I), K(I)/H(I) e NH_4(I)/H(I) facendo uso di titolazioni pHmetriche in condizioni di non equilibrio. I coefficienti di distribuzione di Na(I) e K(I) sono stati determinati in presenza di acidi inorganici a diverse concentrazioni su questi scambiatori ionici. Si è trovato che l'arsenofosfato di cromo possiede una selettività elevata nei confronti dello ione potassio anche in ambiente fortemente acido. Separazioni quantitative di ioni metallici in alcune miscele ternarie ebinarie sono state ottenute su colonna in base alle esperienze di distribuzione.

INTRODUCTION

Much attention has been given to the preparation and ion exchange characteristics of the insoluble arsenates and phosphates of metals with oxidation states higher than 2 over the last twenty years (1-13). Sn(IV) (9,12,13) and Cr(III) (3,4,10,11) salts have been investigated with reference to their ion exchange properties. It has been noted that the double salts of Sn(IV) and Cr(III) show some peculiar characteristics e.g. they are highly stable towards acids and alkalies and retain appreciable ion-exchange capacity at high temperatures (14,15). Because of their reproducible behaviour and ion exchange properties, their utility has been demonstrated for the separation of various metal ions (14-16). We report here a systematic study of the ion exchange behaviour of Sn(IV) and Cr(III) arsenatephosphates towards alkali metal ions and their utility in some analytically important metal separations.

EXPERIMENTAL

Reagents: All reagents and chemicals were either from B.D.H. (England) or of Analar grade; tin(IV) chloride used in these studies was a Polish Product (P.P.H.Polskie Odczynniki Chemiczne Gliwrce).

Apparatus: All pH measurements were made with a digital pH meter model LI-120. Flame photometric studies were made on a Systronics (India) instrument. The X-ray studies were performed on a Philips X-ray unit using Ni-filtered Cu K radiations and Scanning Electron Microscope (SEM) studies were made on a Cambridge Stereoscan Electron Microscope interfaced with an X-ray microprobe analyser.

Preparation of Ion-Exchange Materials: Sn(IV) arsenatephosphate was prepared by mixing 0.1 M solutions of Sn(IV) chloride, sodium arsenate and trisodium orthophosphate in the volume ratio 1:1:1. The pH of the mixture was kept at zero with HNO_3. The gel thus prepared was kept as such at room temperature for 24 hours and then filtered off. It was washed several times with distilled water and dried at 40 °C. The dried material when placed in distilled water, cracked into small granules. They were then put in successive batches of 1 M HNO_3 to convert them into the H(I) form. The material was finally washed with demineralized water to remove excess acid and dried at 40 °C. Granules of the required size were obtained by sieving. Cr(III) arsenatephosphate was prepared by mixing 0.1 M solutions of Cr(III) nitrate, sodium arsenate and trisodium orthophosphate in the volume ratio 2:1:1. The rest of the procedure was as described above. The sodium ion exchange capacities of Sn(IV) and Cr(III) arsenatephosphates determined by column operation were found to be 1.75 and 0.74 mequiv./dry g respectively as reported earlier (14).

Potentiometric Titrations: (a) For Sn(IV) arsenatephosphate: 500 mg of the exchanger were mixed with 100 ml of 0.015 M salt solution (NaCl, KCl, LiCl, or NH_4Cl). This mixture was kept for 1 hour and titrated against 0.015 M solutions of the respective alkali, recording the pH of the solution after each addition of 0.4 ml of the titrant till the pH became constant. The back titration was then carried out by adding the same fractions of 0.015 M HNO_3 to the solution.

(b) For Cr(III) arsenatephosphate: The method followed was as in (a) above except that the concentrations of the salt and alkali solutions was taken as 0.008 M. The back titration was performed by adding 0.008 M HNO_3. The results are summarised in figures 1 and 2.

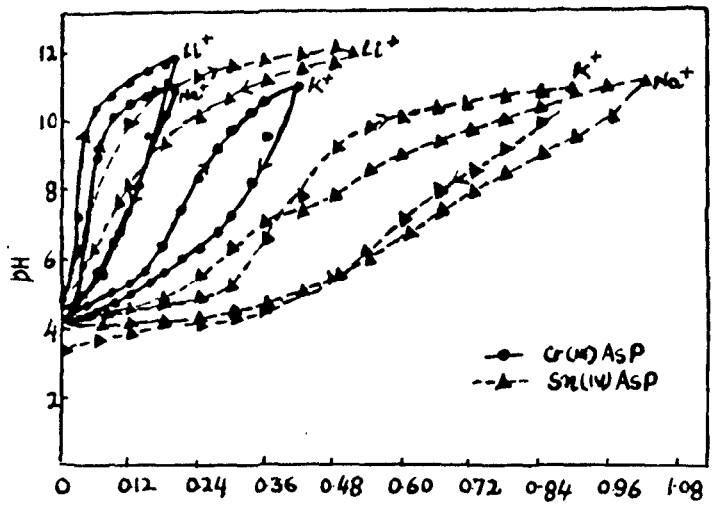


Fig.1. Forward and reverse pH titration curves on Sn(IV) and Cr(III) arsenatephosphates for Li(I)/H(I), Na(I)/H(I) and K(I)/H(I) systems.

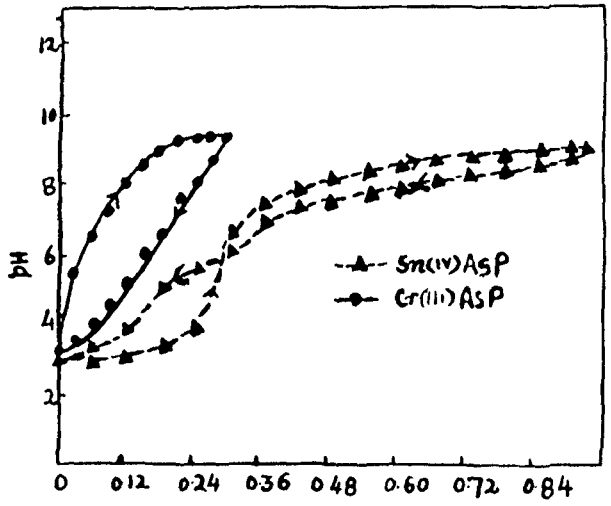


Fig.2. Forward and reverse pH titration curves on Sn(IV) and Cr(III) arsenatephosphates for NH_4(I)/H(I) system.

Distribution studies: The distribution coefficient (K_d) values for Na(I) and K(I) were determined using equation

$$K = \frac{I - F}{F} \times \frac{V}{W}$$

where I = Initial concentration of the metal ion in solution,

F = Final concentration of the metal ion in solution after equilibrium

V = Volume of the solution in contact with the exchanger

W = Weight of the ion exchange material.

Sodium nitrate and potassium nitrate solutions (10^{-4} M) were prepared in demineralized water. Equilibrium was achieved by keeping the solutions over night at room temperature with the ion-exchange material. The amounts of Na(I) and K(I) in the solutions before and after equilibrium were determined by flame photometry.

Separations Achieved: Based on the distribution studies reported earlier (15,16), some separations were tried on columns. For this purpose 1 g of the exchanger was taken in a column, plugged with glass wool and having an internal diameter $\sim$0.6 cm. It was washed

with water and the mixture was loaded and adsorbed at a very slow rate (2-3 drops/minute). Each of the metal ions was eluted out with the selected eluant with a flow rate not exceeding $\sim$ 0.5 ml/minute, analysing every 10 ml fraction for the metal ion content by titrating it against a standard EDTA (0.002 M) solution. The results are summarised in figure 3.

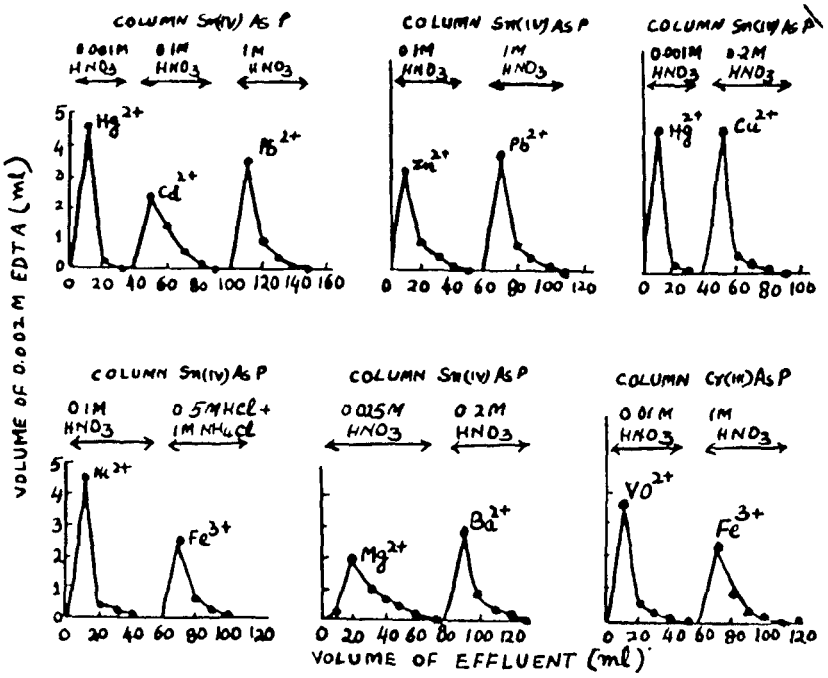


Fig.3. Metal separations on Sn(IV) and Cr(III) arsenatephosphates.

RESULTS AND DISCUSSION

X-ray diffraction and scanning electron microscope studies reveal that both the tin(IV) and chromium(III) arsenatephosphates are amorphous.

Forward and reverse potentiometric titration curves of tin(IV) and chromium(III) arsenatephosphates are shown in Figures 1 and 2. They were obtained under non-equilibrium conditions and hence are different in shape than the ones obtained earlier (14) on the same materials by the equilibrium (batch) process. It may be for this reason that the full ion exchange capacity is not reached in a neutral medium. From these figures it is evident that the uptake of the cations by the host lattice depends on the nature of the counter ions and there are inversions in the selectivity order. For

instance, in the region between pH 3 and 6.5 the tin(IV) arsenatephosphate shows a selectivity sequence as $NH_4(I) > Na(I) > K(I) > Li(I)$, but on increasing the pH (6.5 to 7.5) it alters to $K(I) > Na(I) > NH_4(I) > Li(I)$. A reversal in selectivity order $NH_4(I) > Na(I) > K(I) > Li(I)$ is again found beyond pH 7.5. This behaviour is common in amorphous and poorly crystalline ion exchange materials, and it is difficult to explain without the knowledge of crystal structure (17,18). The amorphous materials have a range of different sized cavities and thus steric effect can explain the change in the selectivity. Surprisingly, chromium(III) arsenatephosphate shows a selectivity order of $K(I) > NH_4(I) > Na(I) > Li(I)$ at all pH values. This observation together with a very low uptake of lithium ion by both materials indicates that the ion exchange occurs by the diffusion of the hydrated counter ion into the ion exchanger, (hydrated radii $Li(I) > Na(I) > K(I)$). This also explains the high uptake of potassium ion shown both in the pH titration curves and in the determination of distribution coefficients in various acidic media (see Table).

TABLE - K_d values of Na(I) and K(I) in water and different concentrations of HNO_3, $HClO_4$ and HCl.

Sl. No.	Solvent	K_d values (ml/g)			
		On Sn(IV) Arsenatephosphate		On Cr(III) Arsenatephosphate	
		For Na(I)	For K(I)	For Na(I)	For K(I)
1	Water	2450	C.A.	330	C.A.
2	1 M HNO_3	26.0	200.0	75.0	C.A.
3	10^{-1} M HNO_3	50.0	450.0	101.0	C.A.
4	10^{-2} M HNO_3	95.0	665	115	C.A.
5	10^{-3} M HNO_3	307	940	158	C.A.
6	10^{-4} M HNO_3	950	1200	177	C.A.
7	10^{-5} M HNO_3	1615	4950	225	C.A.
8	1 M $HClO_4$	110	115	144	108
9	10^{-1} M $HClO_4$	240	198	328	173
10	10^{-2} M $HClO_4$	675	303	675	298
11	10^{-3} M $HClO_4$	1100	498	1192	571
12	10^{-4} M $HClO_4$	1689	1399	2848	1192
13	10^{-5} M $HClO_4$	4298	8646	8646	4298
14	1 M HCl	40.5	150	102	C.A.
15	0.1 M HCl	60.0	290	115	C.A.
16	0.01 M HCl	115	365	175	C.A.
17	0.001 M HCl	305	450	405	C.A.
18	0.0001 M HCl	950	2450	1200	C.A.
19	0.00001 M HCl	2450	C.A.	2450	C.A.

C.A. = Complete Adsorption

These curves also show the hysteresis loop indicating an irreversibility in the ion exchange process. The forward ion-exchange isotherms indicate that the ion exchange capacity for Sn(IV) arsenatephosphate is higher than for the Cr(III) arsenatephosphate. This difference was also noted in the column ion exchange experiment (14). Very strange behaviour has been observed in the reverse titration curve for Sn(IV) arsenatephosphate in the NH_4^+ form. In the lower pH-range the reverse curve is higher than the forward one. This may be due to a higher selectivity for the NH_4(I) ion as compared to the H(I) ion due to its bigger size.

The distribution studies of Na(I) and K(I) on Sn(IV) and Cr(III) arsenatephosphates in different acid media reveal that the nature of the acid plays an important role. Six concentrations (10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} and 1 M) were taken of all these acids and the distribution of both Na(I) and K(I) was observed. Cr(III) arsenatephosphate completely takes up K(I) ion irrespective of the concentration of the acid used while Sn(IV) arsenatephosphate shows a different behaviour for this metal. In this case log K_d values vary linearly with pH having a slope (-p K_d/pH) = 0.25. Almost the same trend is shown for Na(I), but the K_d values are slightly lower than for K(I) at all concentrations. The tendency of both these materials is towards a high selectivity for K(I) in all the acid solutions. Because of this Sn(IV) and Cr(III) arsenophosphates could be used for the separation of K(I) from numerous metal ions. In fact, these materials have already shown (15) their utility for the separation of Na(I) from K(I). Potassium was leached out of the column with a 0.1 M solution of $HClO_4$.

The utility of these materials has also been demonstrated for the separation of other metals. For example a ternary separation involving Pb(II)-Cd(II)-Hg(II) has been achieved on Sn(IV) arsenatephosphate columns. This exchanger has also been found useful for other separations such as Zn(II)-Pb(II), Hg(II)-Cu(II), Ni(II)-Fe(III) and Mg(II)-Ba(II). Cr(III) arsenatephosphate has given a binary separation of VO(II) from Fe(III) using HNO_3 as eluent, which may be useful for the alloy analysis. The separations are quantitative and precise, the experimental error being about + 2%. In order to compare these materials with Sn(IV) arsenate and Sn(IV) phosphate ion exchangers for their separation ability, the latter were prepared by the prescribed (19,20) procedures and some of the separations mentioned above were tried on their columns. It was observed that the ternary separation of Pb(II)-Cd(II)-Hg(II) could not be achieved on these single salts, as Pb(II) is found eluting partially with a 0.1 M HNO_3 solution. The order of elution was, however, found to be the same as on the arsenatephosphate studied here. These substances do not allow to obtain the separation of Pb(II) from Zn(II). Further, Sn(IV) phosphate has mainly been utilised earlier for the separation of fission products, Zr^{95}-Nb^{95} and alkali metals, while our emphasis has been mostly on the common metal ions. Sn(IV) arsenate seems to possess a capability for the separation of Mg(II) from Ba(II) and of Pb(II) from Zn(II) as reported in the literature (19). However, its utility for a ternary separation is still not known unlike our materials.

Acknowledgements - The authors are thankful to Prof.M.Qureshi for research facilities and to the C.S.I.R. (India) for the financial assistance to A.A.K. and P.Das. X-ray and SEM studies were performed at the school of Natural Sciences, Hatifield Polytechnic, U.K.

Received, July 17th, 1980

REFERENCES

1) V.PEKAREK, V.VESLEY: Talanta (Rev), 19, 1245 (1972).
2) M.QURESHI, S.Z.QURESHI, J.P.GUPTA, H.S.RATHORE: Sepn.Science (Rev), 7(6), 615 (1972).
3) G.M.LUKASZEWSKI, J.P.REDFERN, J.E.SALMON: J.Chem.Soc., 39 (1961).
4) G.M.LUKASZEWSKI, J.P.REDFERN: ibid, 4802 (1962).
5) J.P.RAWAT, S.Q.MUJTABA: Canad.J.Chem., 53, 17 (1975).
6) M.QURESHI, J.P.RAWAT, A.P.GUPTA: J.Chromatog., 118, 167 (1976).
7) M.QURESHI, J.P.RAWAT, A.P.GUPTA: Chromatographia, 11, 202 (1978).
8) S.ALLULI, C.FERRAGINA, A.L.GINESTRA, M.A.MASSUCCI, N.TOMASSINI: J.Inorg.Nucl.Chem., 39, 1043 (1977).
9) Y.INOUE: ibid, 26, 2241 (1964).
10) D.BETTERIDGE, G.N.STRADLING: ibid, 29, 2652 (1967).
11) S.W.PAJAKOTT: Montash Chem., 1400 (1968) (Montash).
12) M.QURESHI, J.P.RAWAT: J.Inorg.Nucl.Chem., 30, 305 (1968).
13) M.QURESHI, K.G.VARSHNEY: J.Inorg.Nucl.Chem., 30, 3081 (1968).
14) K.G.VARSHNEY, A.A.KHAN: J.Inorg.Nucl.Chem., 41, 241 (1979).
15) K.G.VARSHNEY, A.A.KHAN: Talanta, 25, 528 (1978).
16) K.G.VARSHNEY, S.NAHEED, A.A.KHAN, S.N.TANDON, C.B.GUPTA: Chromatographia, 12, 473 (1979).
17) C.B.AMPHLETT: "Inorganic ion exchangers", Elsevier, Amsterdam (1964).
18) J.P.GUPTA, D.V.NOWELL, M.QURESHI, A.P.GUPTA: J.Inorg.Nucl.Chem., 40, 545 (1978).
19) M.QURESHI, H.S.RATHORE, R.KUMAR: J.Chem.Soc.(A), 1986 (1970).
20) Y.INONE: Bull.Chem.Soc.Japan, 36, 1324 (1963).

2·15

Distribution Studies of Metal Ions on Arsenophosphates of Sn (IV) and Cr (III) and on Amine Sn (II) Hexacyanoferrates (II) Using Radio Tracers: Separation of Sr^{2+} – Cs^{+}, Hg^{2+} – Ag^{+} and Hg^{2+} – Zn^{2+}

K. G. Varshney / S. Naheed / A. A. Khan

Chemistry Section, Z. H. College of Engineering and Technology, Aligarh Muslim University, Aligarh-202001, India

S. N. Tandon / C. B. Gupta

Chemistry Department, University of Roorkee, Roorkee-247672, India

Key Words

Distribution study
Radio tracer
Metal ions
Ion-exchange

Summary

Distribution studies of some metal ions have been made on Sn(IV) and Cr(III) arsenophosphates and on some samples of Sn(II) amine hexacyanoferrates(II), using radiotracers. The K_d values of Cs^{+} and Rb^{+} have been followed at varying HNO_3 concentrations also. As a result 3 useful binary separations have been achieved on Sn(IV) and Cr(III) arsenophosphates, such as Sr^{2+}–Cs^{+}, Hg^{2+} Ag^{+} and Hg^{2+}–Zn^{2+}.

Introduction

Heteropolyacid salts have received considerable attention because of their peculiar ion-exchange properties. They show, in general, high exchange capacity, reproducibility, high stability and selectivity for metals. Sn(IV) and Cr(III) arsenophosphates have been prepared earlier [1] and studied for their composition, solubility and exchange properties. Amine hexacyanoferrates(II) have been of recent interest especially for the selective adsorption of alkali metals on compounds such as the amine hexacyanoferrates(II), of Co(II) [2], Sn(II) [3] and Sn(IV) [4]. The present paper summarizes a systematic distribution study of various metal ions on these materials using radiotracers. As a result, some useful separations have been achieved.

Experimental

Reagents: All reagents and chemicals were either B.D.H. (England) or of Analar grade. The stannic chloride was a Polish product (I.P.H. Polskie Odezynniki Chemiezne Gliwice, Poland). Ferrocyanic acid was obtained by passing a solution of K_4 $Fe(CN)_6$ over a bed of Amberlite IR-120 in H^{+} form.

Apparatus: All pH-measurements were made on a digital pH-meter model LI-120. Radioisotope measurements were made either on a scintillation counter (γ) or on a G.M. counter (β).

Preparation of Ion-Exchange Materials: Sn(IV) arseno-phosphate was prepared by mixing 0.1 mol dm^{-3} solutions of Sn(IV) chloride, sodium arsenate and trisodium-o-phosphate in the volume ratio 1:1:1. The pH of the mixture was adjusted to zero with HNO_3. The gel thus prepared was kept as such at room temperature for 24 hours and then filtered. It was washed several times with distilled water to remove excess reagents and dried at 40 °C. The dried materials when placed in distilled water decrepitated to small granules. Fines were removed by decantation and the rest placed in 1 mol dm^{-3} HNO_3 for conversion to the H^{+} form. The material was finally washed with demineralized water to pH 6–7, dried at 40 °C and sieved. The Cr(III) arsenophosphate was prepared by mixing the 0.1 mol dm^{-3} solutions of Cr(III) nitrate, sodium arsenate and trisodium-o-phosphate in volume ratio 2:1:1 followed by the above procedure.

The four samples of amine Sn(II) hexacyanoferrates(II) were prepared as follows:

100 cm^3 of 0.1 mol dm^{-3} $K_4Fe(CN)_6$ were passed slowly through a column of cation-exchanger in the H^{+} form. The column was washed with distilled water and the effluent, bluish green in colour was diluted to 250 cm^3. 5 cm^3 of selected amine was added to this solution which was then poured into $SnCl_2$ solution (in 4 mol dm^{-3} HCl) with continuous stirring. The pH of the mixture was adjusted to

0009-5893/79/07 0473-03 $ 02 00/0

≈ 0 with HCl. The precipitates thus formed were digested at room temperature for 24 hours before filtration. They were washed several times to pH 6–7, and dried at 60 °C. The material was allowed to decrepitate into small granules in water and the fines removed by decantation. After drying, the granules were sieved and converted into the H^+ form with 1 to 2 mol dm^{-3} HNO_3 as before. The granules thus obtained were usually black or bluish green in colour. The exchange capacities of all these samples are summarized in Table I.

Table I. Ion exchange capacity of arsenophosphates and hexacyanoferrates(II) prepared

Sample no.	Description	Capacity for Na^+ (mmol/dry g)
S-1	Sn(IV)arsenophosphate	1.75
S-2	Cr(III)arsenophosphate	0.74
S-3	Aniline Sn(II)hexacyanoferrate(II)	1.17
S-4	Ethylamine Sn(II)hexacyanoferrate(II)	1.18
S-5	Pyrrole Sn(II)hexacyanoferrate(II)	1.40
S-6	Piperidine Sn(II)hexacyanoferrate(II)	1.44

Distribution Studies

a) Determination of K_d Values: The K_d values of Hg^{2+}, Zn^{2+}, Rb^+, Sr^{2+}, Co^{2+}, Mn^{2+}, In^{3+}, Y^{3+}, Tb^{3+}, Ag^+, Cs^+ were determined by using radio tracers. Their solutions were adjusted to pH 2 with $HClO_4$. 100 mg of the exchanger were placed in 10 cm^3 each of these solutions (10^{-4} mol dm^{-3}), and equilibrated overnight at room temperature. The activity of the solution was then measured. K_d values were estimated from:

$$K_d = \frac{I - F}{F} \cdot \frac{V}{A} (cm^3/g)$$

where I = initial activity of solution, F = final activity of solution after equilibration, V = total volume of solution, A = weight of exchanger in g.

The results are summarized in Table II.

b) Effect of HNO_3 Concentration on K_d Values: The effect of HNO_3 concentration on K_d values of Cs is shown in Table III.

Table III. Effect of HNO_3 concentration on K_d values of selected samples.

120

Conc. of HNO_3 (mol dm^{-3})	K_d values for Cs^+				
	S-1	S-2	S-3	S-5	S-6
0.001	731	273	890	1962	3675
0.005	370	266	740	1430	3695
0.01	359	164	2179	993	3286
0.05	87	464	1351	1841	400
0.10	–	4676	555	1275	2063

The distribution of Rb^+ was observed by varying the HNO_3 concentration on S-1 samples only. Fig. 1 shows the variation of K_d values with HNO_3 concentration for Cs^+ and Rb^+ on this sample.

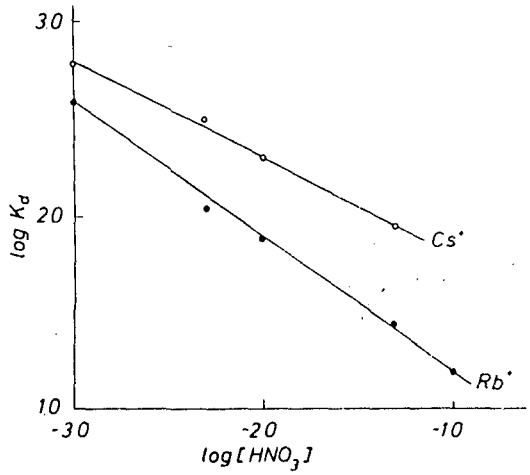


Fig. 1

• Effect of HNO_3 concentration on K_d of Rb^+ and Cs^+ on sample S-1.

Separation Achieved

Three binary separations were achieved on sample S-1: Sr^{2+} - Cs^+, Hg^{2+} - Ag^+ and Hg^{2+} - Zn^{2+}. Sample S-2 was also found to be useful for the separation of Hg^{2+} – Ag^+. 500 mg of the material were packed in a microburette plugged with glass wool; the flow rate was 0.5 cm^3 per minute. The elution curves are shown in Figs. 2–5.

Table II. K_d values at pH 2 on various samples

Sample	Hg^{2+}	Zn^{2+}	Rb^+	Sr^{2+}	Co^{2+}	Mn^{2+}	In^{3+}	Y^{3+}	Tb^{3+}	Ag^+	Cs^+
S-1	2.3	350.6	267.0	16.0	47.8	78.5	30.2	288.1	20.0	391.8	119.3
S-2	6.2	19.6	31.8	0.3	2.4	32.1	94.2	6.4	0.2	217.9	8.6
S-3	60.8	654.0	845.1	27.6	92.4	3.0	75.3	514.2	14.3	518.9	197.7
S-4	56.8	632.1	360.4	13.6	316.0	178.6	600.4	3919.2	487.2	678.3	335.2
S-5	18.2	158.8	703.9	0.3	4.3	12.3	24.3	8.7	0.5	1302.0	287.7
S-6	35.6	1249.0	298.6	17.5	804.8	507.1	68.0	3877.3	0.7	2061.1	293.9

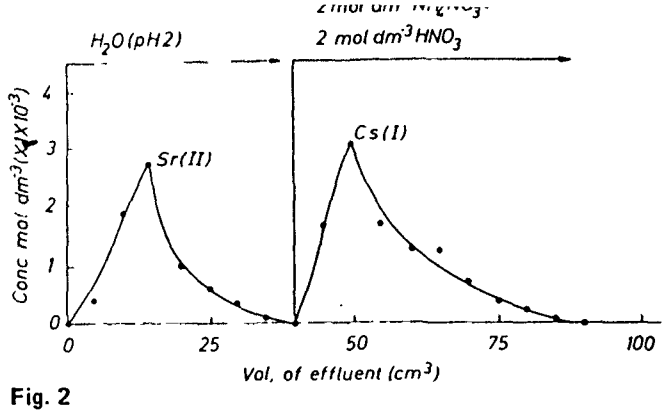


Fig. 2

- Separation of Sr^{2+} from Cs^+ on sample S-1.

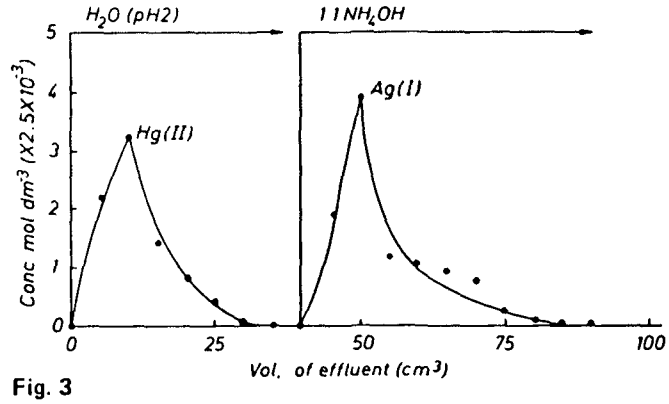


Fig. 3

- Separation of Hg^{2+} from Ag^+ on sample S-1.

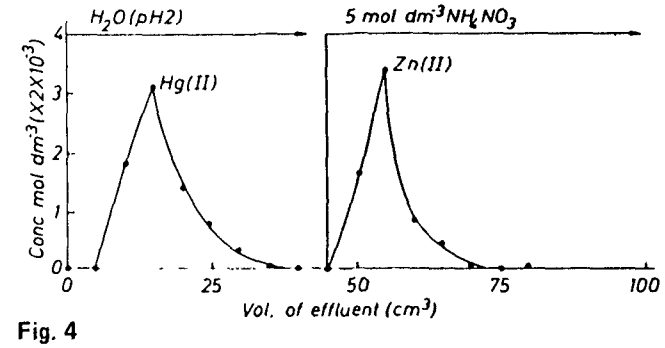


Fig. 4

- Separation of Hg^{2+} from Zn^{2+} on sample S-1.

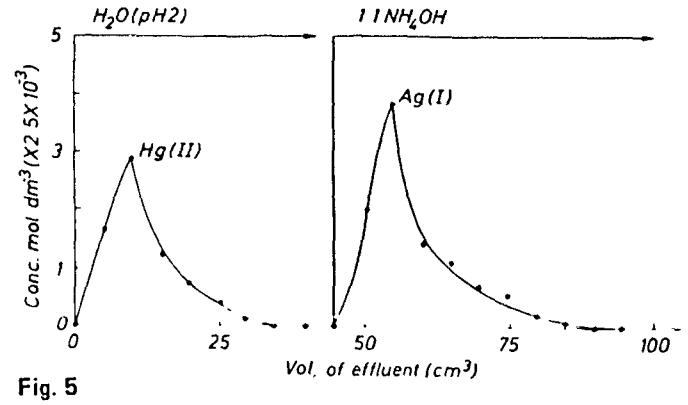


Fig. 5

- Separation of Hg^{2+} from Ag^+ on sample S-2.

Comparison of the distribution of the 11 metals on two samples of arsenophosphates (S-1 and S-2) and four samples of amine hexacyanoferrate (Table II) reveals some interesting features. Thus at pH 2 none of these materials has any affinity for Hg^{2+} and Sr^{2+}. Tb^{3+} is adsorbed only by a sample of amine hexacyanoferrate(II) (S-4). Among the arsenophosphate samples the Sn(IV) salt is found to have appreciable affinity for Zn^{2+}, Rb^+, Y^{3+}, Ag^+, and Cs^+ which is true for the four samples of amine hexacyanoferrates (II) also. Cr(III) arsenophosphate shows a good selectivity for Ag^+. Taking advantage of this behaviour three useful binary separations have been achieved on these samples as mentioned above. Sample S-2 (Cr^{3+} salt), has also been found to be useful for the separation of Hg^{2+}– Ag^+ (Fig. 5). The separation of Sr^{2+} from Cs^+ is of particular interest for fission studies. In U^{235} fission the peaks in the fission-yield curve occur around mass numbers 95 and 138 which is an area corresponding to the nuclides of Sr and Cs respectively. Because of the known stability of inorganic ion-exchangers towards radiation damages, it is appropriate to attempt this separation on these materials. The separations of Hg^{2+}– Zn^{2+} and Hg^{2+} Ag^+ are of normal analytical importance. Such separations have, been attempted and achieved earlier using organic resins but they are more conveniently carried on our materials, as the elution curves are very sharp. On the basis of the distribution coefficient data (Table II) two more separations seem to be possible, Co^{2+}– Mn^{2+} on sample S-3 and Y^{3+}– Tb^{3+} on sample S-6.

Table III summarizes the effect of HNO_3 concentration on the K_d values of Cs^+ on five of these samples. It is interesting to note that a plot of $\log K_d$ vs $\log [HNO_3]$ for this metal is a straight line only for the sample S-1, as shown in Fig. 1. This sample shows linearity for Rb^+ also. However, the slope of these curves is less than 1 (the charge on the metal). This could be because of the simultaneous adsorption of anions on the materials.

Acknowledgement

The authors are thankful to Prof. Mohsin Qureshi, Head, Chemistry Section, Z. H. College of Engineering and Technology, A.M.U., for research facilities. The radio laboratory facilities were provided by the Chemistry Department, University of Roorkee, India.

References

[1] *K. G. Varshney* and *Asif A. Khan*, J. Inorg. Nucl. Chem. (in press).

[2] *R. B. Hahn* and *H. C. Klein*, Anal. Chem. 40, 1135 (1968).

[3] *K. G. Varshney* and *S. Naheed*, J. Inorg. Nucl. Chem. 39, 2075 (1977).

[4] *K. G. Varshney* and *S. S. Varshney* (unpublished studies).

Received: May 17, 1978
Revised Manuscript Received: Aug. 21, 1978
Accepted: Sept. 18, 1978

C

SEPARATION SCIENCE AND TECHNOLOGY, 18(1), pp 59-72, 1983

2·16

Synthesis, Ion-Exchange Behavior, and Analytical Applications of a New, Crystalline, and Stable Zirconium(IV) Arsenosilicate Cation-Exchanger: Analysis of Some Silicate Rocks

K. G. VARSHNEY, SANJAY AGRAWAL, and KANAK VARSHNEY

CHEMISTRY SECTION
ZAKIR HUSAIN COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202001, INDIA

Abstract

A new crystalline inorganic ion exchanger, Zr(IV) arsenosilicate, has been synthesized and shows high chemical and thermal stability. It is also stable under γ-radiations of moderately high strength. The utility of this material has been demonstrated by achieving quantitative separation of Hg(II) from such other metal ions as Cd(II), Pb(II), Ni(II), Co(II), Zn(II), Al(III), and Fe(III) on its columns. Some silicate rocks have also been analyzed using this material.

INTRODUCTION

Silicates and phosphosilicates are generally more stable ion-exchangers both chemically and thermally than other materials of this class (*1–6*). Similarly, arsenates show good ion-exchange capacity and reproducibility in properties (*7–10*). An ion-exchange study of arsenosilicates of tetravalent metals is, however, lacking. Our present efforts are therefore to explore the possibility of preparing different arsenosilicates showing promising ion-exchange behavior and which are stable under high doses of γ-radiations. This article summarizes such a study for the synthesis of a crystalline Zr(IV) arsenosilicate capable of separating Hg(II) from other polluting metal ions. The actual application of the material has been demonstrated in the analysis of some rocks.

 0149-6395/83/1801-0059$3.50/0

EXPERIMENTAL

Reagents

The zirconyl chloride used in this study was a B.D.H. (England) product while the sodium silicate was a Riedel (Dehaenag, Seelze, Hanover) product. All other reagents and chemicals were of AnalaR grade.

Standard Rocks Used

The following rocks obtained (*11*) from the U.S.G.S. (U.S.A.) were analyzed: Andesite (AGV-1), Basalt (BCR-1 and BHVO-1), Granite (G-2), and Periodolite (PCC-1).

Apparatus

pH measurements were made on an Elico (India) Model LI-10 pH meter while IR studies were performed on a Beckman IR-20 spectrophotometer using KBr pellets. X-ray studies were made on a Philips x-ray unit with a Mo-K_α target. Colorimetry was done on a Bausch & Lomb spectronic-20 colorimeter. For thermogravimetric analysis a Modern TGA balance of the Fertilizers Corp. of India Ltd. was used, and for radioisotopic studies a well-type single channel analyzer with a NaI(Tl) detector, obtained from Ecil (India) was used. A Pye Unicam model SP 2900 atomic absorption spectrophotometer was used for the determination of elements in trace amounts.

Preparation of Ion-Exchange Materials

A large number of samples was prepared by varying the concentration and mixing volumes of the various components. However, the sample prepared in the following manner showed high ion-exchange capacity, chemical stability, and reproducibility in properties. An aqueous (0.1 *M*) sodium silicate solution, made acidic (pH 0–1) by adding HCl, was mixed with an aqueous (0.1 *M*) zirconyl chloride solution and the pH of the mixture was raised to 8–10 by the slow addition of ammonium hydroxide with intermittent shaking to obtain a slurry. After filtering and washing with demineralized water (DMW), it was treated with a 1:1 (v/v) mixture of 0.5 *M* solutions of arsenic

and nitric acids. This resulted in a gel which was digested at room temperature for 24 h and then filtered out. It was washed thoroughly to remove excess acid, dried at 45°C, and cracked into small granules by putting in DMW. These were then sieved to obtain 60–100 mesh particles which were converted into the H^+-form using 1 *M* HNO_3. They were finally washed with DMW and dried as usual for further study.

Ion-Exchange Capacity (i.e.c.)

This was determined by the column process using 1 *M* $NaNO_3$ as the eluant and keeping a very slow flow rate (10–12 drops/min) of the effluent. The Na^+-ion exchange capacity of the material was found to be 1.3 meq/dry g.

Thermal Stability

Several 1 g portions of the sample were heated at various temperatures in a muffle furnace for 1 h each and their i.e.c.s were determined as usual after cooling them to the room temperature. The results are summarized in Table 1.

Chemical Stability

250 mg portions of the sample were kept with 25 mL each of the various solvents for 24 h at room temperature with intermittent shaking. The supernatent liquid was then analyzed for the presence of zirconium(IV),

TABLE 1

I.e.c. and General Appearance of ZAS after Heating to Various Temperatures

Heating temperature (°C)	I.e.c. (meq/dry g)	% Retention in i.e.c.	General appearance
45	1.30	100	Dirty white
100	1.30	100	Dirty white
200	1.25	96.2	Dirty white
400	0.46	35.4	White
600	0.20	7.7	White

arsenic(V), and silica using standard colorimetric methods (*12–14*). The results show the negligible amounts of them in the supernatent liquid even on using up to 4*M* acids such as HNO_3, H_2SO_4, HCl, $HClO_4$, and CH_3COOH and 0.1 *M alkali solutions such as NaOH and KOH.*

Composition

100 mg of the powdered sample was dissolved in a minimum amount of H_2SO_4 (conc.). The solution was then diluted to 100 mL with water and the amounts of zirconium(IV), arsenic(V), and silica were determined by standard gravimetric or titrimetric methods (*15–17*). The molar composition of the material was found to be 1:2:1 for Zr:As:Si.

pH Titrations

500 mg of the exchanger was taken in each of several 250 mL conical flasks followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 mL to maintain the ionic strength constant. The pH of the solution was recorded after keeping it for 24 h to attain equilibration, and the pH was plotted against the milliequivalents of the OH^- ions added. Figure 1 shows the pH titration curves for the sample dried at 45°C using different alkalies and their respective chlorides as titrants, while Fig. 2 shows the variation of pH titration curves on heating and irradiating the sample.

TGA, IR, and X-Ray Studies

Figure 3 shows the percent weight loss that occurred in the sample on heating up to 700°C, and Fig. 4 shows the IR spectra of ZAS dried at room temperature and heated at 200°C. X-ray diffraction patterns reveal its crystalline nature and a *d*-value of 2.05 Å.

Distribution Studies

250 mg of the exchanger beads in the H^+ form was equilibrated with 25 mL of the selected solvent, either by shaking for 3–4 h or by keeping at room temperature for 24 h. The initial metal concentration in the solution was adjusted so that it did not exceed 3% of the total i.e.c. of the material. The

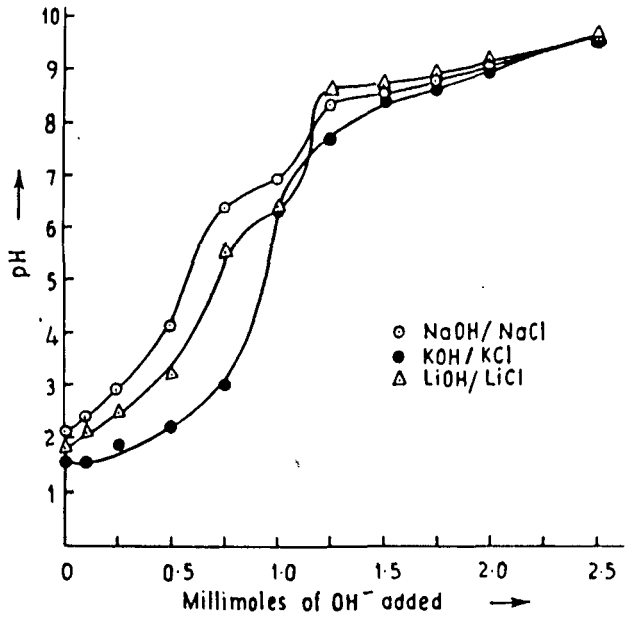


FIG. 1. pH titration curves for ZAS dried at 45 °C using different alkalies and their chlorides as titrants.

determinations were carried out volumetrically using EDTA as the titrant (*18*). For alkali metals the tracer technique was used by employing the following isotopes (half-life periods in parentheses): ^{24}Na (15 h), ^{42}K (12.5 h), ^{86}Rb (18 d), ^{137}Cs (30.2 years).

The K_d values, as summarized in Table 2, were obtained by the equation

$$K_d = \frac{I - F}{F} \times \frac{V}{A} (\text{mL/g})$$

where I = initial amount of the metal ion in the solution phase
F = final amount of the metal ion in the solution phase
V = volume of the solution (mL)
A = amount of the exchanger (g)

The variation of K_d values of alkali metals with pH (fixed with $HClO_4$) is shown in the log K_d vs pH curves of Fig. 5.

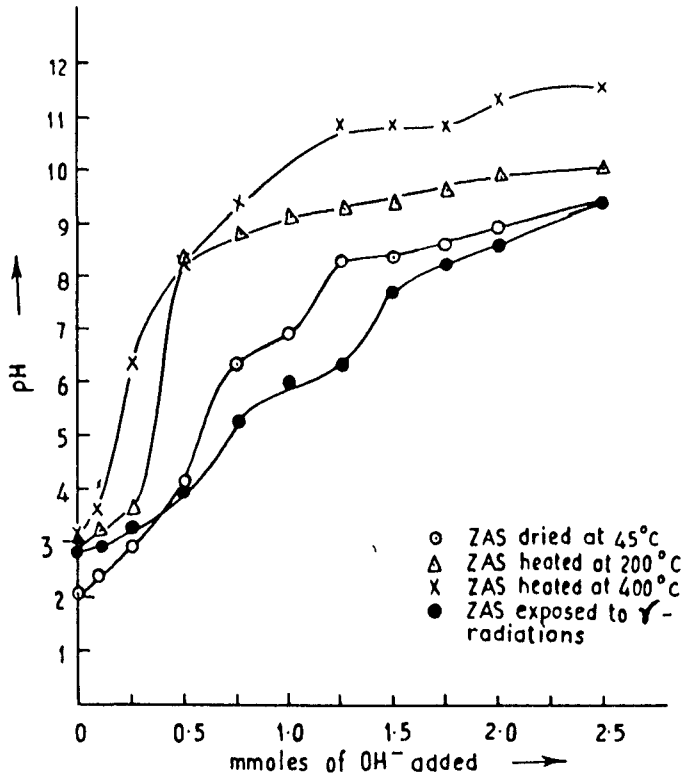


FIG. 2. pH titration curves for ZAS heated at different temperatures and for the irradiated sample using NaOH/NaCl as a titrant

Separations Achieved

In Synthetic Mixtures

The 60–100 mesh sized particles of the exchanger (2 g) in the H^+ form were used for the column operation in a glass tube having an internal diameter of ~0.6 cm. The column was washed thoroughly with DMW and the mixture to be separated was loaded on it, maintaining a flow rate of ~2–3 drops/min. The separation was achieved by passing a suitable solvent through the column as eluant. The metal ions in the effluent were determined quantitatively by EDTA titration. The salient features of the separation of Hg(II) from other metal ions on ZAS columns are summarized in Table 3. A

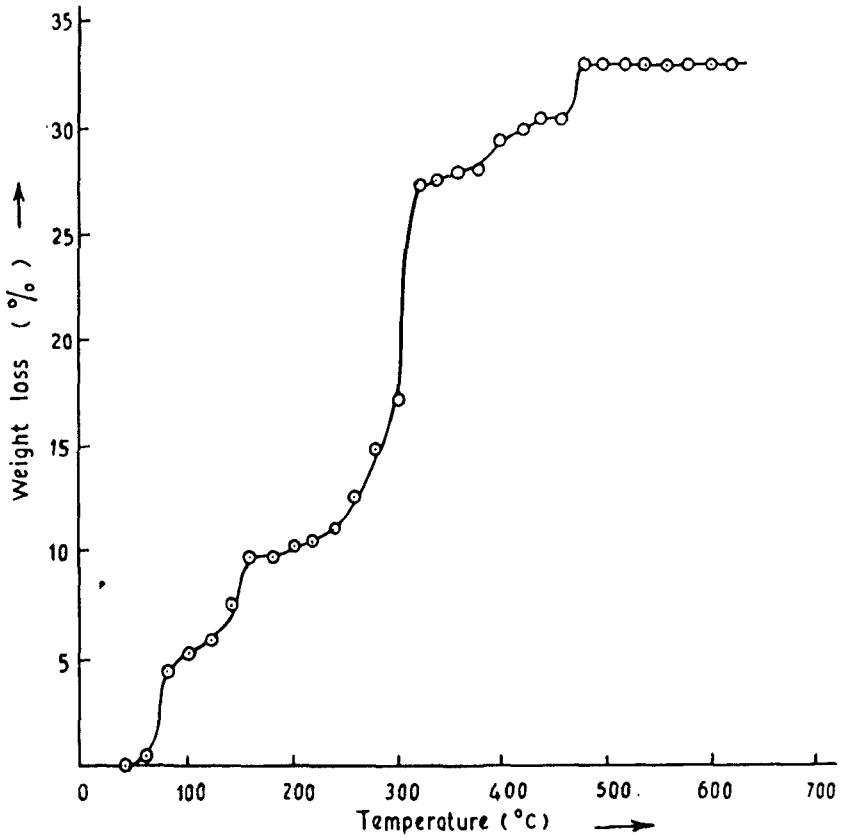


FIG. 3. TGA curve for ZAS in the H^+ form

synthetic mixture was also prepared containing 500 μg Hg(II) with other metal ions such as Cd (280 μg), Pb (520 μg), Zn (160 μg), Ni (180 μg), Co (147.25 μg), and Al (67.5 μg). Hg(II) was quantitatively recovered from this mixture using DMW as the eluant.

In Actual Rock Samples

For preparing standard rock solution, 100 mg of the sample was fused with NaOH in a Ni crucible at dull red heat followed by dissolution of the melt and dilution to a liter with dilute HCl. The analysis was performed as

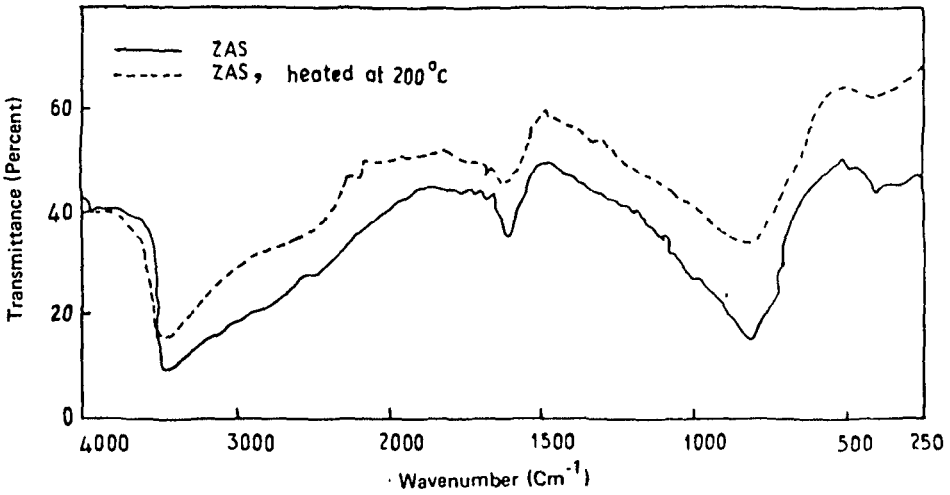


FIG. 4. IR spectra of ZAS dried at 45°C and at 200 C.

follows: 0.5 to 1 mL of the stock solution was evaporated to dryness to remove the excess acids. The residue was taken in DMW (~2 mL) and the solution was applied on the exchanger column (~2 g) as usual. All the elements except Fe and Al were eluted out with DMW. Al and Fe were recovered from the column with 1 *M* HNO_3 as the eluant. The quantitative determination of the elements was done by atomic absorption spectrophotometry. Table 4 summarizes the results.

Irradiation Effect

For such a study the sample was exposed to γ-radiations produced from a ^{60}Co source for 96 h with a dose rate of 0.4 Mrd/h using $FeSO_4$ as a dosimatter. The material was then observed for some of its physical and ion-exchange properties such as appearance, color, grain size, brittleness, i.e.c., elution behavior, K_d values, and pH titration. No change was reported in any of the above properties except the last one which is affected very slightly (Fig. 2).

DISCUSSION

The material obtained in these studies, Zr(IV) arsenosilicate, shows a cation-exchange capacity comparable with other materials of this class. It

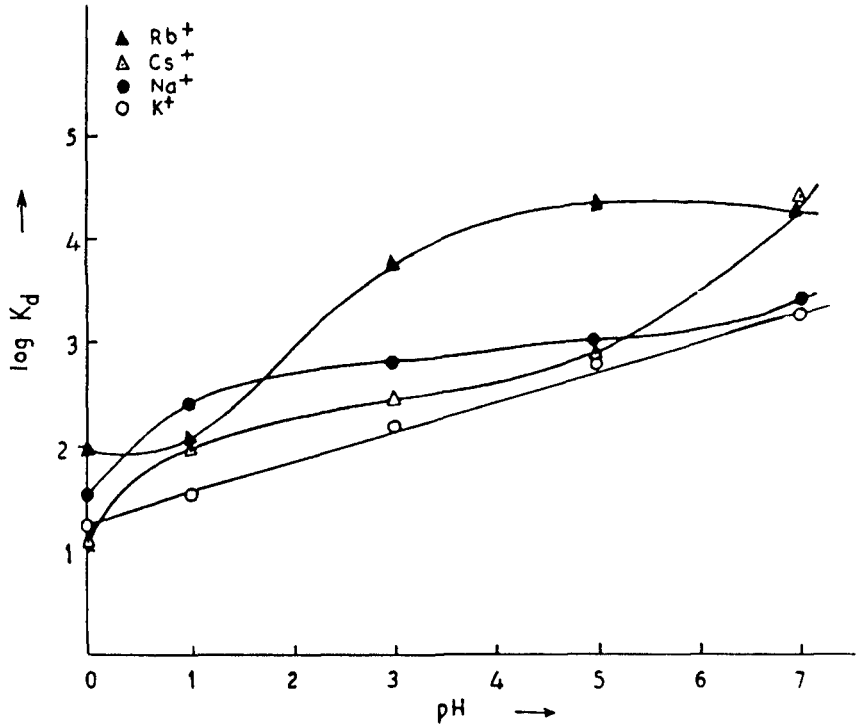


FIG 5 Effect of pH on the K_d values of alkali metals on ZAS

TABLE 2

K_d Values of Some Common metal Ions in Different Media for ZAS

Metal ions	DMW ($X \times 10^{-2}$)	0.01 *M* HNO_3 ($X \times 10^{-2}$)	0.1 *M* HNO_3 ($X \times 10^{-2}$)	0.01 *M* $HClO_4$ ($X \times 10^{-2}$)	0.1 *M* $HClO_4$ ($X \times 10^{-2}$)
Ba(II)	1.10	1.05	0.91	3.00	1.63
Cd(II)	80.3	1.86	1.30	2.13	1.40
Pb(II)	54.3	15.8	14.6	54.3	54.3
Mg(II)	3.67	0.77	0.63	0.46	0.37
Sr(II)	2.18	0.35	0.03	0.41	0.13
Hg(II)	0.52	0.58	0.41	0.75	0.52
Mn(II)	0.69	0.13	0.09	0.20	0.13
Ca(II)	3.14	0.81	0.36	0.74	0.23
Zn(II)	10.0	0.57	0.36	0.57	0.26
Ni(II)	80.0	2.06	1.90	1.78	1.10
Co(II)	6.00	7.00	4.09	4.33	2.50
Al(III)	43.5	38.8	3.20	7.09	3.50
Fe(III)	38.5	2.93	2.10	1.26	0.97

TABLE 3

Some Binary Separations Involving Hg(II) on ZAS Columns

No.	Separations achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluant used	Volume of the eluant used (mL)
		500 Hg	500 Hg	0	DMW	40
1	Hg(II)–Cd(II)					
		280 Cd	280 Cd	0	0.1 *M* HNO_3	50
		500 Hg	487 Hg	−2.6	DMW	
2	Hg(II)–Pb(II)					
		520 Pb	520 Pb	0	0.1 *M* HNO_3 + 1 *M* NH_4NO_3	90
		500 Hg	500 Hg	0	DMW	
3	Hg(II)–Zn(II)					
		160 Zn	157 Zn	−1.9	0.1 *M* HNO_3	40
		500 Hg	500 Hg	0	DMW	30
4	Hg(II)–Ni(II)					
		180 Ni	179 Ni	−0.6	0.1 *M* HNO_3	70
		500 Hg	500 Hg	0	DMW	40
5	Hg(II)–Co(II)					
		147.25 Co	142 Co	−3.5	0.1 *M* HNO_3 + 1 *M* NH_4NO_3	50
		500 Hg	500 Hg	0	DMW	30
6	Hg(II)–Al(III)					
		67.5 Al	67.5 Al	0	0.5 *M* HCl + 1 *M* NH_4Cl	30
		500 Hg	500 Hg	0	DMW	40
7	Hg(II)–Fe(III)					
		125 Fe	123.3 Fe	−1.36	0.5 *M* HCl + 1 *M* NH_4Cl	40

shows a high reproducibility in its ion-exchange behavior and a crystalline nature with a d-value of 2.04 Å. When the material was heated at various temperatures ranging from 45 to 800°C for 1 h each, it was observed that up to 200°C the i.e.c. is lost only up to 4%. The solubility studies of this exchanger in various acids and alkali solutions suggest that it is quite stable in these media. The irradiation studies reveal that ZAS is stable under γ-radiations up to 38.4 Mrd.

The pH titration curves (Figs. 1 and 2) indicate an expected bifunctional behavior of the exchanger except for K^+ ions, for which a monofunctional behavior is observed. The second inflection for the sample ZAS, dried at room temperature, is at about 1.1 mmol of OH^- ions added, corresponds approximately to the experimentally obtained Na^+–i.e.c. of the material (Fig. 2). The samples heated at 200 or 400°C, however, lose their bifunctional characteristics, as is evident from Fig. 2. The IR spectrum of the ZAS sample (Fig. 4) shows sharp and strong bands at ~800, ~1600, and ~3500 cm^{-1} which justify the presence of arsenate, silicate, and external water molecules in the structure.

Distribution studies show a normally good selectivity of this material for various metal ions in water, which is usual for inorganic ion-exchangers. As it is clear from Fig. 5, the exchanger shows a reversal in K_d values for alkali metals on varying the pH. At pH ~ 0 the material shows the sequence $Cs^+ < K^+ < Na^+ < Rb^+$.

Thus it shows a maximum uptake for Rb^+ at this pH. However, at pH 1 the exchanger shows a high selectivity for Na^+ ions. At pH 7 a further reversibility is observed in its behavior, for there the exchanger shows a maximum affinity for Cs^+ ions. On the basis of distribution studies and individual elution curves of different metal ions, binary separations of Hg(II) from Cd(II), Pb(II), Ni(II), Co(II), Zn(II), Al(III), and Fe(III) have been successfully obtained, the details of which are summarized in Table 3. When a synthetic mixture containing Hg(II) and other metal ions (Cd, Pb, Ni, Co, Zn and Al) was loaded on its column, Hg(II) could be eluted out quantitatively in DMW. This study, therefore, points out the possibility of utilizing Zr(IV) arsenosilicate for some metal separations that are important from the pollution point of view. Analysis of rocks is another exciting application of this material. As Table 4 shows, quite satisfactory results are obtained within an experimental error of ±5%.

Acknowledgments

The authors thank Prof Mohsin Qureshi for research facilities. Dr S. C. D. Sah, Director, Wadia Institute of Himalayan Geology, Dehradun, India, is

TABLE 4

Quantitative Separation of Various Constituents in Rocks on ZAS Columns

No		Volume of the stock solution loaded (mL)	Elements present as per the standard composition of the rock (μg)						Elements eluted out in various solvents (μg) (arrange values of three determinations) Eluants and their volumes		% Error for Al and Fe
			Al	Fe	Si	Ca	Mg	Mn	DMW (100 mL)	1 M HNO_3 (100 mL)	
1	G-2	0 5	7 70	1 35	34 61	0 98	0 375	0 020	Si (37 82) Ca (1 07) Mg (0 41)	Al (7 92) Fe (1 40)	Al +2 85 Fe +4 47
2	G-2	1 0	15 40	2 69	69 22	1 96	0 75	0 03	Si (74 11) Ca (2 02) Mg (0 79)	Al (15 8) Fe (2 76)	Al +2 59 Fe +2 60
3	AGV-1	0 5	8 60	3 89	29 81	2 47	0 76	0 05	Si (33 4) Ca (2 52) Mg (0 81) Mn (0 08)	Al (8 63) Fe (3 82)	Al +0 46 Fe −1 79
4	AGV 1	1 0	17 19	7 78	59 61	4 94	1 52	0 10	Si (64 15) Ca (5 04) Mg (1 64) Mn (1 01)	Al (17 4) Fe (7 7)	Al +1 22 Fe −1 02

5	BHVO-1	0.5	6.85	6.00	2.45	7.7	3.60	0.08	Si(2.45) Ca(7.81) Mg(3.39) Mn(0.08)	Al(6.96) Fe(6.16)	Al +1.6 Fe +2.66
6	BHVO-1	1.0	13.7	12.0	4.9	15.4	7.20	0.17	Si(5.18) Ca(15.65) Mg(7.32) Mn(0.16)	Al(14.2) Fe(11.85)	Al +3.64 Fe −1.25
7	BCR-1	0.5	6.86	6.71	27.26	3.48	1.74	0.09	Si(26.95) Ca(3.56) Mg(1.84) Mn(0.08)	Al(7.1) Fe(6.74)	Al +3.49 Fe +0.01
8	BCR-1	1.0	13.72	13.41	54.53	6.97	3.48	0.18	Si(13.84) Ca(6.88) Mg(3.37) Mn(0.16)	Al(13.96) Fe(13.62)	Al +1.74 Fe +1.56
9	PCC-1	0.5	0.36	4.14	21.05	0.27	21.75	0.06	Si(22.34) Ca(0.4) Mg(22.2) Mn(0.08)	Al(0.35) Fe(4.11)	Al −2.77 Fe −0.72
10	PCC-1	1.0	0.73	8.28	42.1	0.55	43.5	0.12	Si(44.7) Ca(0.83) Mg(44.15) Mn(0.14)	Al(0.72) Fe(8.14)	Al −1.36 Fe −1.69

thanked for providing the rock analysis facilities in his institute Financial assistance was provided by the C.S I R., India

REFERENCES

1 T P Tang, P Sun, and K Y Chan *Hua Hsueh* p 33 (1965)
2 T P Tang, P Sun, and K Y Chan, *Ibid*, p 9 (1967)
3 D Naumann, *Kernenergie, 6,* 173 (1963)
4 K G Varshney and A A Khan, *J Inorg Nucl Chem*, *41,* 241 (1979)
5 K G Varshney and A Premadas, *J Liq Chromatogr*, *4,* 915 (1981)
6 K G Varshney and A Premadas, *Ibid*, *4* 1245 (1981)
7 E Torracca, U Costantino, and M A Massucci *J Chromatogr*, *30* 584 (1967)
8 G Alberti, U Costantino, F di Gregorio, and E Torracca *J Inorg Nucl Chem 31,* 3195 (1969)
9 G Alberti and M A Massucci *Ibid*, *32,* 1719 (1970)
10 M Qureshi, R Kumar, and H S Rathore *J Chem Soc*, *A* p 272 (1970)
11 S Abbey, *Geostand Newslett 4* 163 (1980)
12 F D Snell and C T Snell *Colorimetric Methods of Analysis* Vol 2 3rd ed Van Nostrand Princeton, New Jersey 1959, p 448
13 E B Sandell, *Colorimetric Determination of Traces of Metals,* Vol 3 Interscience New York, 1959, p 282
14 W W Scott, *Standard Methods of Chemical Analysis,* 5th ed , Van Nostrand New York 1939, p 803
15 N H Furman *Standard Methods of Chemical Analysis,* Vol 1, 6th ed Van Nostrand Princeton, New Jersey, 1963, p 1270
16 Ref *14* p 117
17 A I Vogel, *Textbook of Quantitative Inorganic Analysis* 4th revised ed Clav (The Chaucer Press), Bungay, 1978, p 501
18 C N Reilley, R W Schmid, and Fawzys, *J Chem Educ*, *36,* 555 (1959)

Received by editor July 26, 1982

Indian Journal of Technology
Vol 22, March 1984, pp. 99-103

2.17 Synthesis of a New Thermally Stable Sn(IV) Arsenosilicate Cation Exchanger and Its Application for the Column Chromatographic Separation of Metal Ions

K G VARSHNEY, A A KHAN, A MAHESHWARI, S ANWAR & U SHARMA

Chemistry Section, Z H College of Engineering and Technology
Aligarh Muslim University, Aligarh 202001 India

A new amorphous phase of inorganic ion exchange material, Sn(IV) arsenosilicate, has been prepared and its ion exchange behaviour studied. Based on the distribution studies of different metals, some important separations of metal ions have been obtained using radiotracers. A tentative formula of the material has also been proposed on the basis of its chemical analysis, *p*H-titration, infrared and thermogravimetric data.

Silica-based double salts are useful cation exchangers as they generally show a high chemical and thermal stability. Phosphosilicates of Zr(IV), Ti(IV), Ce(IV), and Sn(IV), have been prepared[1-4] and their ion exchange properties studied along with their separation potential. As the literature shows, arsenosilicates of tetravalent metals have still not been studied for their ion-exchange behaviour. It was, therefore, decided to prepare an arsenosilicate of Sn(IV) and to study its ion-exchange properties in order to explore its separation potential for metal ions.

Experimental Procedure

Reagents and chemicals—Stannic chloride used in these studies was a product of P.P.H. Polskie Odezynniki Chemiezire Gliwica, Poland. All other reagents and chemicals were either from BDH (England) or E. Merck (Darmstadt G.F.R.).

Apparatus—For *p*H measurements an Elico model LI-10 *p*H meter was used and infrared studies were made on a Perkin-Elmer Model 621 Infrared grating spectrophotometer. Thermogravimetric analysis was performed on a TGA balance of FCI (India). Radioisotopic measurements were made either on a scintillation counter (for γ-radiations) or on a G.M. counter (for β-radiations).

Preparation of the materials

(a) *Using sodium arsenate*—Solutions of sodium silicate, sodium arsenate and $SnCl_4$ were mixed in a volume ratio of 1:1:1 and the *p*H of the gel produced was set at 1 with HNO_3. The slurry was then kept at room temperature for 24 hr and filtered. After washing with demineralized water (DMW) several times to remove excess reagents the gel was dried at 45°C and was placed in water to crack it into small grannules. After further washing with DMW to a *p*H 6-7, the granules were placed in 1 mol/dm^3 HNO_3 for 24 hr to convert them into the H^+ form. After removing the excess acid they were dried at 45°C. This sample will be termed as SAS-1.

(b) *Using arsenic acid*—A definite volume of sodium silicate solution was added to conc. HCl (5 ml per 100 ml Na silicate solution) followed by the same volume of aqueous stannic chloride solution. The *p*H of the mixture was adjusted to 9-10 by adding NH_4OH and the resultant slurry was allowed to stand overnight. It was filtered, washed with DMW and mixed with the same volume of the H_2AsO_3-HNO_3 mixture (1 mol/dm^3 in terms of each acid). The gel thus obtained was then heated as described in (a) to obtain the granules which will be termed as SAS-2.

Composition—500 mg of the exchanger was boiled with 20 ml HCl to dissolve arsenate and tin present in the compound. Undissolved silica was filtered out and determined gravimetrically[5]. H_2S gas was passed through the filtrate to precipitate tin and arsenic as sulphides which were treated with HCl to dissolve tin. Tin was then determined[6] volumetrically with $K_2Cr_2O_7$ and the undissolved precipitate containing arsenic was dissolved in NaOH, and titrated against thiocyanate[7]. The molar composition of the compound was 1:1:1 for Sn, As and Si.

Ion-exchange capacity—The material was found to be a cation-exchanger and hence its ion-exchange capacity was determined using different metal solutions by the column process as usual. 1 g exchanger was taken for the column preparation and the flow rate was maintained at 0.5 ml/min using 1 mol/dm^3 solutions of the eluants. The ion-exchange capacity of the sample SAS-1 for different metal salts is given below (in meq/dry g):

$NaNO_3$(0.95), KNO_3(0.95), $Ca(NO_3)_2$(1.40) $Sr(NO_3)_2$ (1.30), $Ba(NO_3)_2$(1.20).

The Na^+-ion exchange capacity for SAS-2 was 1.25 meq/dry g.

Concentration and elution curves—The amount of the H^+ ions eluted from the column depends on the concentration of the eluant. It was observed that 1 mol/dm^3 solution of $NaNO_3$ was sufficient to elute almost all the H^+ ions from a column containing 1 g ion exchanger when an arbitrarily fixed volume, say 125 ml, was taken of the eluant. This concentration was therefore used to obtain the elution curve which shows that the complete elution of H^+ ions is obtained in only 50 ml of the eluant.

Chemical and thermal stability—The apparent chemical stability was observed in HNO_3 and NaOH of different concentrations. The exchanger was found fairly stable when kept overnight in 1 mol/dm^3 HNO_3 and 0.01 mol/dm^3 NaOH. However, it dissolved appreciably in 0.05 mol/dm^3 and stronger NaOH solutions.

For thermal stability 1 g exchanger was kept at various temperatures for 1 hr each and the Na^+ ion-exchange capacity was determined as usual after cooling the samples to room temperature The results are summarized in Table 1 for both the samples SAS-1 and SAS-2.

pH-titrations—They were carried out by the method of Topp anc Pepper[8] and the results are shown in Fig. 1 for the sample SAS-2.

Table 1—Ion-Exchange Capacity of Sn(IV) Arsenosilicate (SAS-1 and SAS-2) after Heating to Various Temperatures

Drying temperature °C	Ion-exchange capacity	
	For SAS-1 meq/g	For SAS-2 meq/g
45	0.95	1.25
100	0.65	1.20
200	0.60	1.11
400	0.50	1.03
600	0.20	0.92
800	0.00	0.68

IR and TGA studies—The IR spectrum of the sample obtained against the Nujol blank is shown in Fig. 2 and the TGA curves are shown in Fig. 3.

Distribution studies

(a) *Determination of K_d values*—Distribution studies for 14 metal ions were performed in dilute solutions of HNO_3, $HClO_4$, HCl and in DMW by taking 250 mg of exchanger (SAS-1 and SAS-2) in a conical flask containing 25 ml of the solution whose metal ion concentration was adjusted to ~3% of the total ion-exchange capacity of the material. The equilibrium was attained by keeping the solutions overnight, and the metal ions left in the solution were determined with EDTA[9]. The K_d values were then calculated as usual[10] and are summarized in Table 2.

The distribution coefficients of some metal ions were also determined using radiotracers in aqueous solution of *p*H 2 adjusted with $HClO_4$ (Table 3). For this, 100 mg of the exchanger (SAS-1) was equilibrated

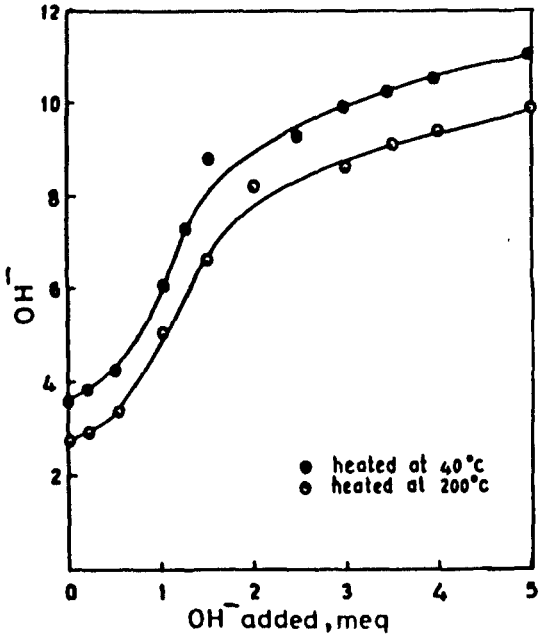


Fig. 1—*p*H titration curve for Sn(IV) arsenosilicate (SAS-2)

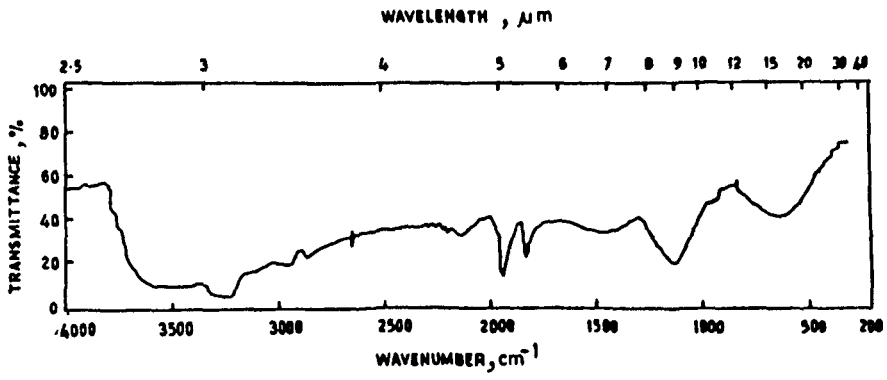


Fig. 2—IR spectrum for Sn(IV) arsenosilicate (SAS-1)

Table 2— Distribution Coefficients of Some Metal Ions on Sn(IV) Arsenosilicate (SAS-1 and SAS-2)

Metal ions	$K_d \times 10^{-2}$													
	DMW*		10^{-2}mol/dm^3 HCl		10^{-1}mol/dm^3 HCl		10^{-2}mol/dm^3 HNO_3		10^{-1}mol/dm^3 HNO_3		10^{-2}mol/dm^3 $HClO_4$		10^{-1}mol/dm^3 $HClO_4$	
	SAS-1	SAS-2	SAS-1	SAS-2	SAS-1	SAS-2	SAS-1	SAS-2	SAS-1	SAS-2	SAS-1	SAS-2	SAS-1	SAS-2
Zn(II)	1.90	3.46	0.00	0.00	0.00	0 00	0.06	1.52	0 01	0 00	0 00	2.39	26 6	0.00
Cd(II)	0.05	2.60	0.00	0.00	0.00	0.00	0 00	0.80	0 01	0 00	0 00	0 75	0.00	0.00
Mg(II)	0.08	1.15	0.00	0.00	0.00	0.00	0.26	0.98	0.58	0 00	0 00	1.06	0.00	0.00
Ba(II)	10.3	1.26	3.90	2.20	3.90	0 13	0 00	0 88	10 3	0 10	1.95	2.16	3.90	0 00
Ca(II)	0.90	5.53	0.00	1.15	0.12	0.00	0 00	5 48	0 96	0 00	0 00	1.38	0 00	0 16
Sr(II)	0.44	2.00	0.20	1.64	0.44	0.10	0 00	2.30	1 25	0 06	3 40	1 64	0 00	0 02
Mn(II)	5.40	1.67	0.00	2.20	0.69	0.17	0.00	3.57	0 68	0 14	0 00	3.21	0.68	0.14
Ni(II)	2.71	3.64	0.19	1.32	0.03	0.00	0 85	0.16	0 96	2.57	0 00	4 16	0 00	3 64
Co(II)	0.24	1.63	35.0	6.73	0.24	1.62	3.00	2.37	1.44	1 62	0 19	4 30	0.36	3 72
Fe(III)	0.19	0.19	0.31	1.13	0.42	0.42	0.00	2.20	0.95	0 00	0.19	1.13	0.42	0.07
Hg(II)	10.9	2.69	1.64	32.2	0.54	3.74	0.46	32.2	22.6	5.64	2.41	32 2	1.90	5.64
Pb(II)	0.95	0.00	3.25	0.00	1.00	0.00	1.00	0.00	3 25	0 00	0 24	0.00	3.78	0.00
Cu(II)	3.35	1.74	0.00	0.37	0.65	0.37	0.07	1.40	0 60	0 28	0 00	0.40	0 95	1 29
Al(III)	2.81	5.24	6.62	2.51	0.05	2.31	2.39	3.08	1.77	3 08	5 80	7.55	2.75	3.08

* Demineralized water

Table 3—Distribution Coefficients of Some Metal Ions in $HClO_4$ Solution (*p*H-2) Using Radiotracers

Metal ions	Distribution coefficients $K_d \times 10^{-1}$
Cs(I)	8.45
Rb(I)	9.16
Tl(I)	1.31
In(II)	0.95
Y(III)	36.5
Tb(III)	7.50
Cr(III)	44.5

with 10 ml each of the labelled solutions and the radioactivity of the solution was recorded after filtration. The initial radioactivity of the solution being known the K_d values were calculated by the formula:

$$K_d = \frac{1-F}{F} \times \frac{V}{M}$$

where F is the fraction of the activity present in the solution after equilibrium, V is the volume of the solution in ml, and M is the mass of the exchanger in g. Fig. 4 shows the variation of K_d values with *p*H for Cs^+ ion.

Separations achieved—Several binary separations were tried using a column containing 2 g of the exchanger (100-200 mesh) in H^+ form taken in a glass tube having an i.d. of 0.6 cm. The metal ions were eluted at a flow rate of 0.1 ml/min using eluants selected on the basis of K_d-value experiment. The metal ions in the effluents were determined as described above. The important separations achieved on its columns are shown in Fig. 5.

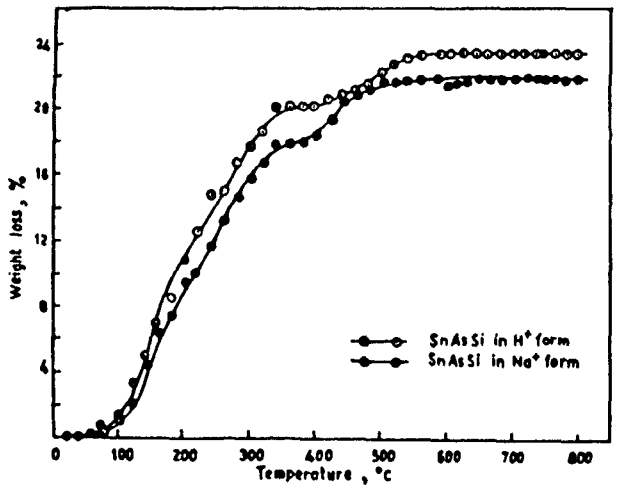


Fig. 3—TGA curves for Sn(IV) arsenosilicate in H^+ and Na^+ forms (SAS-1)

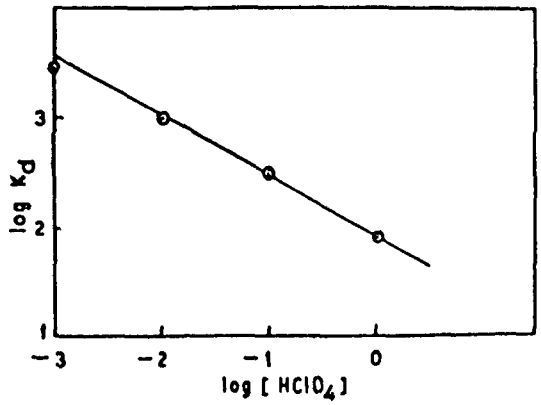


Fig. 4—Effect of $HClO_4$ on K_d values of Cs^+ on Sn(IV) arsenosilicate (SAS-1)

Discussion

The main features of this study are:

1. The synthesis of a new ion-exchange material based on tin (IV), arsenic (V) and silicon(IV), showing a very high thermal stability.

2. Separation of metal ions important from the analytical and pollution point of view using liquid column chromatography.

Sn(IV) arsenosilicate shows a cation-exchange behaviour similar to other materials of this class prepared earlier. It is clear from Table 1 that the material obtained by using arsenic acid as one of the components (SAS-2) exhibits a better ion-exchange capacity than the one prepared with Na-arsenate. The method of precipitation of SAS-2 involved an effective arsenatization similar to that of Ce(IV) and Sn(IV) phosphosilicates prepared earlier[3,4]. The silicic acid obtained on adding HCl to a clear solution of sodium silicate forms a gel when treated with $SnCl_4$ at $pH = 9$. This gel probably consists of flakes[11] of SiO_2 coated with $Sn(OH)_4$. Protogenic arsenate groups are then attached to the matrix when this gel is treated with a mixture of H_2AsO_3-HNO_3. This difference in the procedure of precipitation has given a striking difference in its thermal stability. Sample SAS-2 retains about 50% of its total ion-exchange capacity even at 800°C while sample SAS-1 loses it sharply on heating (Fig. 6). Sample SAS-2 can be ranked with Zr(IV) arsenophosphate[11] and Sb(V) silicate[10] in its thermal stability.

The IR spectrum (Fig. 2) shows the bands at ~600, 1100, 1800, 2000 and 3300-3700 cm^{-1}. The first two bands indicate the presence of arsenate[12] in the structure, in addition to the metal-oxygen stretching vibrations (M-O) which also absorb in this range. The presence of Si-O-Si open chains or rings in the structure and the Si-OH stretching vibrations are evidenced by the absorption bands near the 1100 cm^{-1} and 3300 cm^{-1} ranges respectively. The frequency band at 3300-3700 cm^{-1} also represents the region in which external water molecules absorb.

The TGA curves of this salt (Fig. 3) show that the percent weight loss in the sample in H^+-form is greater than that in Na^+-form. It is obviously because of the presence of more protons in the structure of the former material. The weight loss in the substance up to 340°C includes the removal of external water molecules and excess of As_2O_5[13] from the structure. The condensation, which might have begun after this temperature probably continues up to about 500°C as is evident from the fact that the weight becomes constant after this temperature. On the basis of its chemical analysis, thermogravimetry and infrared studies the following formula may be proposed tentatively for the material:

$$[SnO_2.H_3AsO_4.SiO_2].nH_2O$$

The value of n (number of external water molecules per molecule of the exchanger) comes out to be 3.4 by Alberti's method[14], if it is assumed that up to 200°C only external water molecules are removed. A further heating up to 350°C might remove the extra As_2O_5

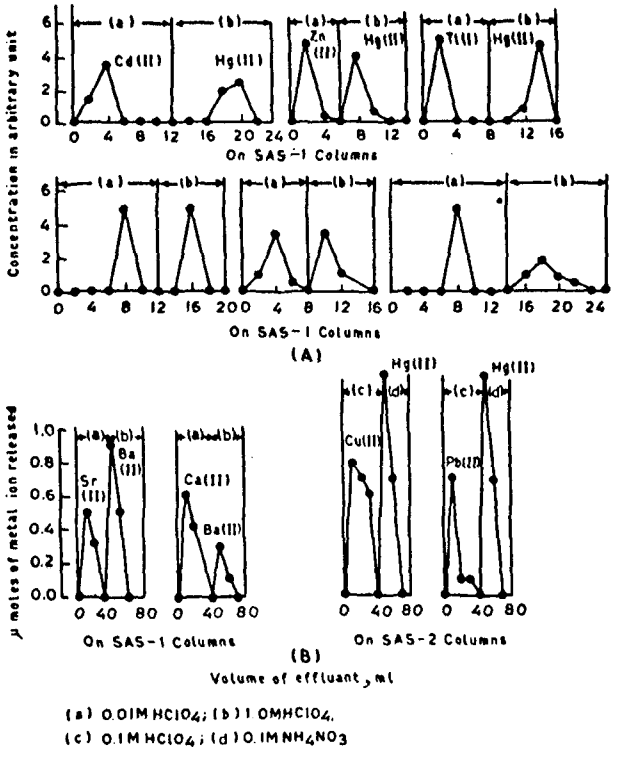


Fig. 5—Some binary separations on Sn(IV) arsenosilicate columns: (A) using radiotracer technique; (B) using EDTA titration method

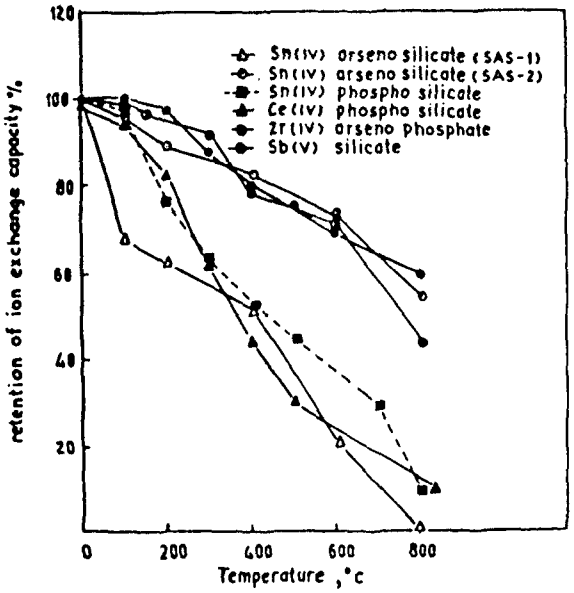


Fig. 6- A comparison of the thermal stability of Sn(IV) arsenosilicate with other similar materials

from the total mass of the exchanger, thus accounting for an additional 5% weight loss.

Table 2 illustrates the K_d values of 14 metal ions in DMW, HCl, HNO_3 and $HClO_4$ for samples SAS-1 and SAS-2. A reversal in the distribution behaviour for some common metal ions is observed which may be due to the difference in their methods of preparation. Thus, while SAS-1 shows a high selectivity for Ba(II), Mn(II) and Hg(II), SAS-2 is selective for Ca(II) and Al(III) in DMW. Also, an unusually high K_d value is observed for Hg(II) on SAS-2 in 10^{-2} mole dm^{-3} HCl, HNO_3 and $HClO_4$ solutions. Effect of $HClO_4$ concentration on the distribution behaviour for Cs(I) ion is shown in Fig. 4, which is a usual phenomenon. This figure also indicates a high selectivity of this material for Cs(I) ion. Based on these observations some important binary separations have been achieved on the columns of samples SAS-1 and SAS-2 (Fig. 5). These separations demonstrate well the analytical and industrial utility of Sn(IV) arsenosilicate.

Acknowledgement

We thank the Council of Scientific and Industrial Research, New Delhi for financial assistance. We are grateful to Prof. S N Tandon, Department of Chemistry, University of Roorkee, for his valuable suggestions and kind help in some radiochemical studies.

References

1 Naumann D, *Kernenergie*, 6 (1963) 173.
2 Naqvi S J, Huyes D & Baetsle L H, *J Inorg Nucl Chem*, 33 (1971) 4317.
3 Varshney K G & Premadas A, *J Liquid Chromatog*, 4 (1981) 915.
4 Varshney K G & Premadas A, *J Liquid Chromatog*, 4 (1981) 1245.
5 Vogel A I, *Text-book of quantitative inorganic analysis*, 4th edn, 1978, 501.
6 Kolthoff I M & Belcher R, *Volumetric analysis*, Vol 3 (Interscience, New-York) 1938, 196.
7 Furman N H, *Standard methods of chemical analysis* 6th edn, Vol 1, (Van Nostrand, Princeton) 1963, 117.
8 Topp N E & Pepper K W, *J Chem Soc*, (1949) 3299.
9 Reilley C N, Schmid R W & Fawzys, *J Chem Educ*, 36 (1959) 555.
10 Varshney K G, Sharma U, Rani S & Premadas A, *Sep Sci Technol*, 17 (1982) 1527.
11 Varshney K G & Premadas A, *Sep Sci Technol*, 16 (1981) 793.
12 Rao C N R, *Chemical applications of infrared spectroscopy* (Academic Press, New York) 1963, 288.
13 Duval C, *Inorganic thermogravimetric analysis*, IInd revised edn, (Elsevier, Amsterdam, New York) 1963, 203.
14 Alberti G, Torraca E & Conte A, *J Inorg Nucl Chem*, 28 (1966) 607.

Colloids and Surfaces, 29 (1988) 175-189
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2·18

Synthetic, Kinetic and Analytical Studies on Titanium(IV) Arsenosilicate Ion Exchanger: Separation of Lead from its Synthetic Alloys

K.G. VARSHNEY, KANAK AGRAWAL, SANJAY AGRAWAL, VIRENDRA SAXENA and A.R. KHAN

Analytical Laboratory, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh-202001 (India)

(Received 23 April 1987; accepted in final form 27 July 1987)

ABSTRACT

Titanium(IV) arsenosilicate has been synthesized as a new cation exchanger and has been characterized on the basis of its chemical composition, ion-exchange behaviour, pH titrations, TGA, IR and X-ray studies. On the basis of the distribution studies, the exchanger was found to be highly selective for lead and, hence, has been used for the separation of this metal ion from some synthetic lead alloys. A kinetic study has also been conducted for the exchange of some heavy pollutants.

INTRODUCTION

Inorganic ion exchangers have recently been utilized in some novel applications [1-4] such as in the analysis of rocks, minerals and pharmaceuticals. The separation of pollutants is important from the point of view of environmental studies. Lead is an important pollutant, the main sources of its poisoning being lead joints of cast iron pipes, lead pipes used for connecting plumbing fixtures, wash basins, kitchen sinks, lead paints used for painting steel water storage tanks and lead compounds used as stabilizers in some plastic pipes. This report describes the synthesis and ion-exchange properties of titanium(IV) arsenosilicate cation exchanger which is highly selective for lead. This ion exchanger has been further utilized in the separation of this metal from its synthetic alloys such as solder, pewter, Wood's metal, Lipowitz alloy, Rose's metal and Newton's metal. A kinetic study was also carried out on the interaction of this material with some heavy metal pollutants such as Mn(II), Fe(III), Co(II), Ni(II), Cd(II), Zn(II), Hg(II) and Pb(II), in order to understand the mechanism of exchange.

0166-6622/88/$03.50

EXPERIMENTAL

Chemicals

Titanium tetrachloride used in this study was a product of Fluka AG, Chemische Fabric, CH-9470 Buchs, while sodium metasilicate and arsenic acid were obtained from the B.D.H., Poole (England). All other reagents were of Analar grade.

Instruments/apparatus used

pH measurements were made on an Elico Model LI-10 pH meter (India) while IR studies were performed on an IR-20 spectrophotometer. An X-ray diffraction unit with a Cu-K_α target was used for X-ray studies and a Cahn thermobalance (Model 2050) was used for TGA. A shaking water-bath incubator with a temperature variation of $\pm 0.5°C$ was used for the equilibrium studies.

Synthesis of titanium(IV) arsenosilicate

Various samples of titanium(IV) arsenosilicate (TAS) were prepared by mixing aqueous solutions of titanium(IV) chloride, arsenic acid and sodium silicate at different concentrations and volume ratios. The sample selected for detailed study because of its good ion-exchange capacity and chemical stability was obtained by the following procedure.

Solutions of $TiCl_4$ (0.1 *M*), H_3AsO_4 (0.2 *M*), $Na_2SiO_3 \cdot 5H_2O$ (0.1 *M*) and HNO_3 (1 *M*) were mixed in equal volume ratios with constant stirring and the resultant gel was kept at room temperature (30°C) overnight. It was then filtered, washed with demineralized water (DMW) till pH 5, and dried at 40°C in an air oven. The dried product (TAS) was immersed in DMW to obtain small granules which were converted to the H^+ form by placing it in 0.1 *M* HNO_3 for few hours. The Na^+ ion-exchange capacity of this sample, determined by the usual column method, was found to be 1.26 meq/dry g.

When the slurry obtained as indicated above was refluxed for 100 h in ~4 *M* HNO_3 a crystalline material (TAS*) was obtained as revealed by the X-ray studies. However, this new sample possesses a negligible ion-exchange capacity.

Thermal/chemical stabilities

Thermal stability was studied by heating 1-g samples of the material at various temperatures for 1 h in a muffle furnace and then cooling them to room temperature. Their ion-exchange capacity was determined by the usual column procedure as summarized in Table 1.

TABLE 1

Ion-exchange capacity of titanium(IV) arsenosilicate after heating to various temperatures

Drying temperature (°C)	Time of heating (h)	Na^+ ion-exchange capacity (meq/dry g)	% Retention of ion-exchange capacity
80	1	1.26	100
200	1	0.90	71
300	1	0.85	67
400	1	0.72	57
600	1	0.05	4
800	1	0	0

Chemical stability was determined on 250-mg portions of the sample kept in 25 ml of various solvents for 24 h with intermittent shaking. 5 ml of the supernatant liquid was evaporated to dryness and redissolved in 25 ml of DMW. Titanium, arsenic and silicon were then determined separately by the following methods.

Determination of titanium

5 ml of the solution was mixed with 0.3 ml of a 30% H_2O_2 solution and the volume was made 25 ml by adding 10% H_2SO_4 in a volumetric flask. Absorbance of the colour was measured at 410 nm against the reagent blank [5].

Determination of arsenic

The molybdenum blue method was employed [6]. The reagent solution was prepared by mixing 10 ml of solution A (1 g ammonium molybdate dissolved in 100 ml of 5 *N* H_2SO_4) with 1 ml of solution B (0.150 g hydrazine sulphate dissolved in 100 ml of DMW) and diluting the mixture to 100 ml. This solution was prepared fresh daily. 10 ml of this reagent were added to the sample solution (5 ml) and the mixture was heated on a steam bath for 15 min. After cooling, it was transferred to a 25 ml volumetric flask and diluted upto the mark with the reagent solution. The absorbance was read at 850 nm against the reagent blank.

Determination of silicon

5 ml of the solution was mixed with 0.5 ml of 10% aq. ammonium molybdate and 0.1 ml of 50% H_2SO_4. The solution was diluted upto 25 ml in a volumetric flask and the absorbance was read at 420 nm against the reagent blank [7].

Table 2 summarizes the results of these chemical analyses.

TABLE 2

Chemical stability of titanium(IV) arsenosilicate in various solvents

Solvent (25 ml)	Amount of TAS dissolved (mg)		
	Ti	As	Si
DMW	0.00	0.00	0.00
1 *M* HNO_3	14.00	24.00	6.00
0.5 *M* HNO_3	1.40	0.60	0.06
1 *M* H_2SO_4	14.00	12.00	6.00
0.5 *M* H_2SO_4	7.00	6.00	3.00
0.1 *M* H_2SO_4	1.40	0.60	0.06
1 *M* HCl	14.00	24.00	6.00
0.5 *M* HCl	3.50	12.00	3.00
0.1 *M* HCl	1.40	0.90	0.09
2 *M* $HClO_4$	2.03	0.60	0.00
1 *M* $HClO_4$	1.40	0.00	0.00
1 *M* CH_3COOH	0.00	0.48	0.00
1 *M* HCOOH	0.00	0.59	0.00
0.1 *M* NaOH	0.00	0.92	0.30
0.05 *M* NaOH	0.00	0.92	0.06
0.1 *M* KOH	0.31	0.97	0.10
1 *M* NH_4NO_3	0.00	0.00	0.11
1 *M* $NaNO_3$	0.31	0.00	0.12

Characterization of materials

Chemical composition

250 mg of the powdered sample were dissolved in a minimum amount (~ 10 ml) of conc. H_2SO_4 and the solution was diluted to 100 ml with water. The amounts of titanium(IV), arsenic(V) and silicon(IV) were determined by standard methods [8,9] which indicated molar ratios of 2:1:3 and 2:1:1 in the amorphous and crystalline phases, respectively. Thus, the crystalline form is different in chemical composition from the amorphous form. The latter decomposes on prolonged heating giving 2 mol of insoluble SiO_2.

pH titrations

500 mg of the exchanger (H^+ form) were placed in each of several conical flasks containing 50 ml mixtures of the solutions of metal chlorides and their corresponding hydroxides in different volume ratios to maintain the ionic strength constant. The pH values were recorded at equilibrium which was attained after overnight incubation with intermittent shaking. Figure 1 shows

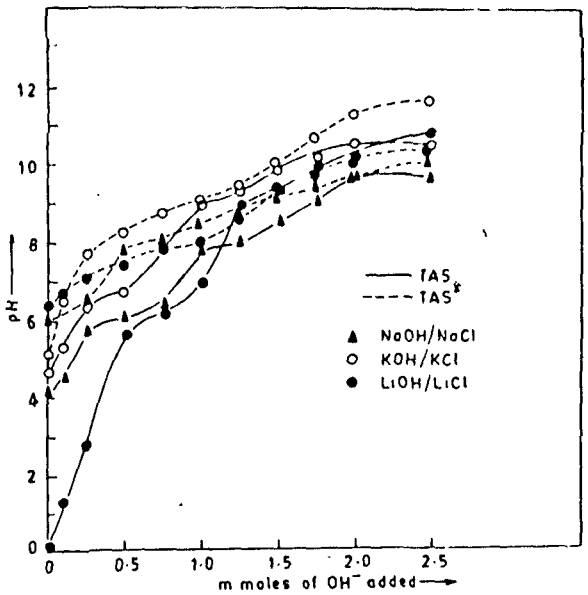


Fig. 1. pH titration curves for TAS and TAS* using different titrant systems.

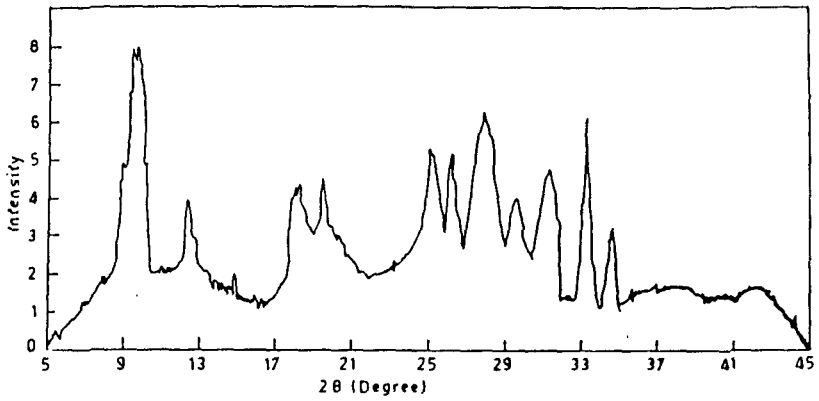


Fig. 2. X-ray diffraction pattern of TAS*.

the plots of pH versus mmol of OH^- added, for TAS and TAS* using NaOH/NaCl, KOH/KCl and LiOH/LiCl systems.

X-ray, IR and TGA studies

X-ray diffraction patterns indicated that the sample of TAS is amorphous while TAS* is crystalline (Fig. 2) with d values of 9.3015, 7.1320, 4.9238, 4.5715, 3.5309, 3.3984, 3.1839, 3.0155, 2.8465, 2.6882 and 2.5902.

IR and TGA curves are shown in Figs 3 and 4, respectively.

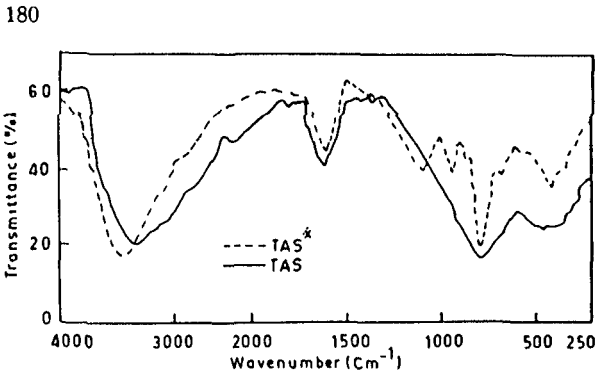


Fig. 3. Infrared spectra of TAS and TAS* in H^+ form.

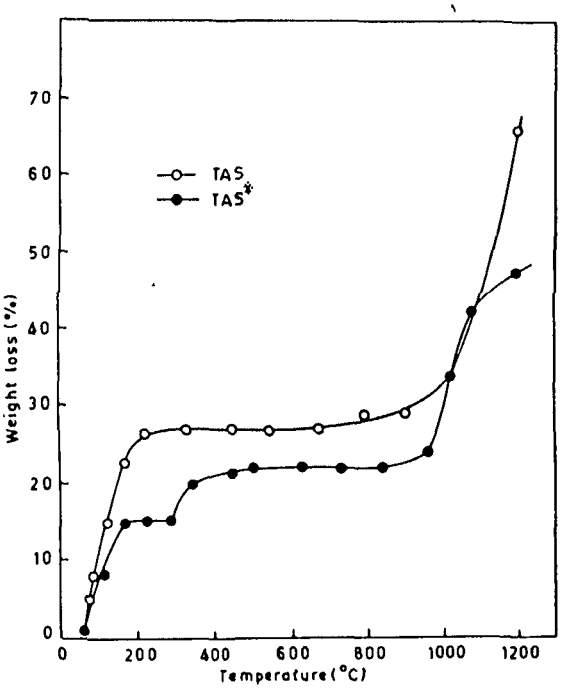


Fig. 4. Thermogram of TAS and TAS*.

Distribution studies

Since the crystalline phase did not show any ion-exchange capacity, the distribution behaviour of only the amorphous sample was studied. It was determined for the 14 heavy metal ions in DMW, HNO_3 and $HClO_4$ media, using the batch process: 250 mg of the exchanger (H^+ form) were shaken with 25 ml of the metal solution in selected media at room temperature for 5–6 h to attain equilibrium. Distribution coefficients (K_d) were obtained by the relation

COLSURF 29/2 katem 3

TABLE 3

Distribution coefficients of some metal ions with titanium(IV) arsenosilicate in water, HNO_3 and $HClO_4$ media

Metal ions	$K_d \times 10^{-2}$				
	DMW	0.01 *M* HNO_3	0.1 *M* HNO_3	0.01 *M* $HClO_4$	0.1 *M* $HClO_4$
Mg(II)	0.23	0.00	0.00	0.00	0.00
Ca(II)	0.45	0.06	0.00	0.09	0.00
Sr(II)	0.10	0.00	0.00	0.00	0.00
Ba(II)	2.3	0.00	0.00	0.00	0.00
Mn(II)	0.60	0.00	0.00	0.00	0.00
Fe(III)	4.0	2.0	1.7	0.00	0.00
Ni(II)	0.23	0.00	0.00	0.00	0.00
Cu(II)	2.0	0.14	0.00	0.28	0.10
Zn(II)	0.60	0.00	0.00	0.00	0.00
Cd(II)	1.5	0.00	0.00	0.00	0.00
Hg(II)	0.50	0.00	0.00	0.00	0.00
Sn(II)	0.12	0.00	0.00	–	–
Pb(II)	TA[a]	TA[a]	1.0	5.3	4.00
Bi(III)	0.21	0.00	0.00	–	–
Al(III)	1.11	0.60	0.11	0.00	0.00

[a]TA, total adsorption.

$$K_d = \frac{(1-F)}{F} \times \frac{V}{M}$$

where F is the fraction of the total metal ion concentration in the solution phase, V is the volume (ml) of the solution and M is the mass (g) of the exchanger. The results are summarized in Table 3.

Separation of Pb(II) from other metal ions

For the column operation, TAS (2 g, H^+ form, 60–100 mesh BSS) was packed in a glass tube (i.d. ~0.6 cm) with a glass wool plug at the bottom. The column was washed with DMW and loaded with the mixture (2 ml) to be separated. 0.01 *M* HNO_3 was used for the elution of Mg(II), Ca(II), Ba(II), Sr(II), Mn(II), Ni(II), Zn(II), Cd(II), Hg(II), Sn(II) and Bi(III), while 0.01 *M* $HClO_4$ was used for Fe(III) and Al(III). Pb(II) was eluted out by a 1 *M* NH_4NO_3 solution. The effluents were analyzed for metal ion content using EDTA titrations. The flow rate was maintained at ~0.5 ml min^{-1} in each case. Table 4 summarizes the details of the binary separations achieved on column.

A few synthetic mixtures were also prepared by mixing metal ion solutions in ratios corresponding to the standard compositions of some lead alloys. Pb(II)

TABLE 4

Some binary separations achieved involving Pb(II) on TAS columns

Sample No	Separations achieved	Amount loaded (μg)	Amount Recovered (μg)	% Error	Eluent used	Volume of the eluent used (ml)
1	Pb(II)-Mg(II)	730 Mg	742 Mg	+1.6	0.01 *M* HNO_3	40
		4140 Pb	4122 Pb	−0.43	1 *M* NH_4NO_3	90
2	Pb(II)-Ca(II)	1200 Ca	1200 Ca	0	0.01 *M* HNO_3	60
		4140 Pb	4140 Pb	0	1 *M* NH_4NO_3	80
3	Pb(II)-Sr(II)	1750 Sr	1731 Sr	−1.6	0.01 *M* HNO_3	70
		4140 Pb	4140 Pb	0	1 *M* NH_4NO_3	80
4	Pb(II)-Ba(II)	750 Ba	750 Ba	0	0.01 *M* HNO_3	90
		4140 Pb	4111 Pb	−0.70	1 *M* NH_4NO_3	70
5	Pb(II)-Mn(II)	2900 Mn	2850 Mn	−1.72	0.01 *M* HNO_3	100
		4140 Pb	4100 Pb	−0.96	1 *M* NH_4NO_3	80
6	Pb(II)-Ni(II)	2935 Ni	2900 Ni	−1.2	0.01 *M* HNO_3	110
		4140 Pb	4100 Pb	−0.96	1 *M* NH_4NO_3	90
7	Pb(II)-Zn(II)	1960 Zn	1942 Zn	−0.92	0.01 *M* HNO_3	110
		4140 Pb	4188 Pb	+1.2	1 *M* NH_4NO_3	70
8	Pb(II)-Cd(II)	2250 Cd	2281 Cd	+1.4	0.01 *M* HNO_3	100
		4140 Pb	4092 Pb	−1.2	1 *M* NH_4NO_3	80
9	Pb(II)-Hg(II)	10030 Hg	9850 Hg	−1.8	0.01 *M* HNO_3	100
		4140 Pb	4140 Pb	0	1 *M* NH_4NO_3	90
10	Pb(II)-Sn(II)	5935 Sn	5900 Sn	−0.59	0.01 *M* HNO_3	110
		4140 Pb	4012 Pb	−1.2	1 *M* NH_4NO_3	70
11	Pb(II)-Bi(III)	10449 Bi	10229 Bi	−2.1	0.01 *M* HNO_3	100
		4140 Pb	4188 Pb	+1.2	1 *M* NH_4NO_3	80
12	Pb(II)-Fe(III)	2800 Fe	2890 Fe	+3.21	0.01 *M* $HClO_4$	100
		4140 Pb	4092 Pb	−1.2	1 *M* NH_4NO_3	80
13	Pb(II)-Al(III)	1350 Al	1400 Al	+3.73	0.01 *M* $HClO_4$	110
		4140 Pb	4092 Pb	−1.2	1 *M* NH_4NO_3	90

was separated from these mixtures following the procedure described above and the results are shown in Table 5.

Kinetic measurements

TAS was well ground and passed through standard sieves to obtain different mesh sizes (10–25, 25–50, 50–70, 70–100 and 100–150). Particles of mesh size 50–70 were generally used unless stated otherwise. 20-ml fractions of the metal ion solutions, (Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg and Pb) were shaken with 200 mg of the exchanger in H^+ form in several stoppered conical flasks at the desired temperatures (20, 30, 45 and 60 ± 0.5°C) for different time intervals.

TABLE 5

Quantitative separation of lead from some synthetic lead alloys on TAS columns

Synthetic alloy and its composition (μg) per ml of stock solution	Amount of Pb obtained in the effluent (μg)	% Error
Solder (Pb, 500; Sn, 500)	496.8	−0.64
-do- (Pb, 430; Sn, 570)	434.7	+1.1
Pewter (Pb, 250; Sn, 750)	253.6	+1.4
Fusible alloys		
Wood's metal (Pb, 250; Sn, 125; Bi, 500; Cd, 125)	243.2	−2.7
Lipowitz alloy (Pb, 270; Sn, 130; Bi, 500; Cd, 100)	274.3	+1.6
Rose's metal (Pb, 280; Sn, 220; Bi, 500)	284.6	+1.6
Newton's metal (Pb, 310; Sn, 190; Bi, 500)	315.7	+1.8

Supernatant liquid was immediately removed and analyzed for its metal ion content.

RESULTS AND DISCUSSION

The main feature of these studies was to prepare a new inorganic ion exchanger, Ti(IV) arsenosilicate, both in the amorphous and crystalline form. As the results show, the sample TAS* which is highly crystalline in nature, has negligible ion-exchange capacity as compared to the amorphous TAS — an unusual phenomenon considering earlier reports of materials found to have enhanced ion-exchange properties with improvement of their crystalline nature [10]. A prolonged refluxing might have removed the highly protogenic groups of arsenic acid (K for $H_3AsO_4 = 6.0 \times 10^{-3}$) as compared to those of silicic acid (K_1 for $H_4SiO_4 = 1.3 \times 10^{-11}$).

TAS appears to be quite stable thermally. It retains approximately 57% of its ion-exchange capacity even after heating upto 400°C as shown in Table 1. It also appears chemically stable as evident from Table 2.

Based on the chemical composition, ion-exchange behaviour, pH titration, IR and TGA studies, the formulae of the crystalline and amorphous titanium (IV) arsenosilicate can be written tentatively as:

TAS*: $(TiO_2)_2 \cdot (HAsO_3) \cdot (SiO_2) \cdot mH_2O$

and

TAS: $(TiO_2)_2 \cdot (H_3AsO_4) \cdot (H_2SiO_2)_3 \cdot nH_2O$

The external water molecules (m, n) in the two cases can be determined by the formulae

$$18m = \frac{X\,(M+18m)}{100}$$

and

$$18n = \frac{X\,(M+18n)}{100}$$

where X is the percent loss of water from the exchanger while $(M+18m)$ and $(M+18n)$ are the theoretical molecular weights of TAS* and TAS, respectively.

If one assumes that the external water is completely removed on heating the sample upto $\sim 170°C$, then the percent loss of water at this temperature as indicated in the TGA curves (Fig. 4) to be 15 for TAS* and 22 for TAS yields values of 3.4 and 8.4 for m and n, respectively. A further loss of weight beyond 170°C may be due to the condensation of the molelcule with the removal of exchangeable protons. The peaks at 500, 900, 1600 and 3500 cm^{-1} in the IR spectrum are indicative of the metal–oxygen, arsenate, silicate and water molecules, respectively, in the material.

The pH titration curves (Fig. 1) show a very interesting feature of the material. The crystalline phase shows a smaller release of H^+ ions as compared to the amorphous phase obviously because of a lower ion-exchange capacity of the former. In addition, there is a reversal in the adsorption behaviour for alkali metals. The amorphous phase shows an extraordinary, high adsorption for Li(I) ions at a low pH, the order being Li(I) > Na(I) > K(I). The order changes to Na(I) > K(I) > Li(I) as the pH increases. In the case of the crystalline phase, however, the adsorption order is K(I) > Na(I) > Li(I) at lower pH and Na(I) > Li(I) > K(I) at higher pH values. Furthermore, the curves indicate a bifunctional behaviour of the material which is due to the large difference in the dissociation constants of the two protogenic groups, namely the arsenic and silicic acids in the material.

On the basis of the distribution studies (Table 3), lead can be separated on a column of TAS from several metal ions such as Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Ni(II), Zn(II), Cd(II), Hg(II), Sn(II), Al(III), Fe(III) and Bi(III), the details of which are summarized in Table 4. Table 5 further illustrates the potential of this material in the separation of Pb(II) from some synthetic lead alloys. This is important from the pollution point of view. Since the material is fairly stable in dilute acid solutions (Table 2), it poses no danger due to the presence of arsenic in its matrix.

Kinetic measurements were made under conditions favouring a particle-diffusion-controlled ion-exchange phenomenon. The fractional attainment of equilibrium U_t may be expressed as:

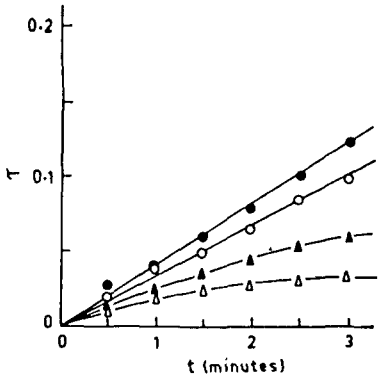


Fig. 5. Plots of τ versus t for H(I)-Cu(II) exchange using different solution concentrations at 30°C on titanium(IV) arsenosilicate (TAS): (△) 0.008 *M*; (▲) 0.01 *M*; (○) 0.03 *M*; (●) 0.05 *M*.

$$U_\tau = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time, i.e. at equilibrium}}$$

Using this expression the mean values of U_τ (six replicate measurements, standard deviation $< 15 \times 10^{-3}$ abs.) were obtained for different time intervals and at different temperatures. Each value of U_τ has a corresponding value of τ which is obtained from the equation:

$$U_\tau = \{1 - \exp[\pi^2 (f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{\frac{1}{2}}$$

where $\tau = \bar{D}_H t / r_0^2$ and the mobility ratio is $\alpha = \bar{D}_H / \bar{D}_M$, r_0 is the particle radius and $\bar{D}_M$ is the interdiffusion coefficient for the metal ion. $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as follows:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.14}}$$

The effect of concentration on the rate of exchange was studied at 30°C using different metal ion concentrations (0.008, 0.01, 0.03 and 0.05 *M*) for Cu(II). The plots of τ versus t (Fig. 5) at the Cu(II) concentrations ≥ 0.03 *M* are straight lines passing through the origin, confirming a particle-diffusion-controlled exchange at these concentrations. A metal ion concentration of 0.05 *M* was therefore selected for the measurement of all kinetic parameters. The τ

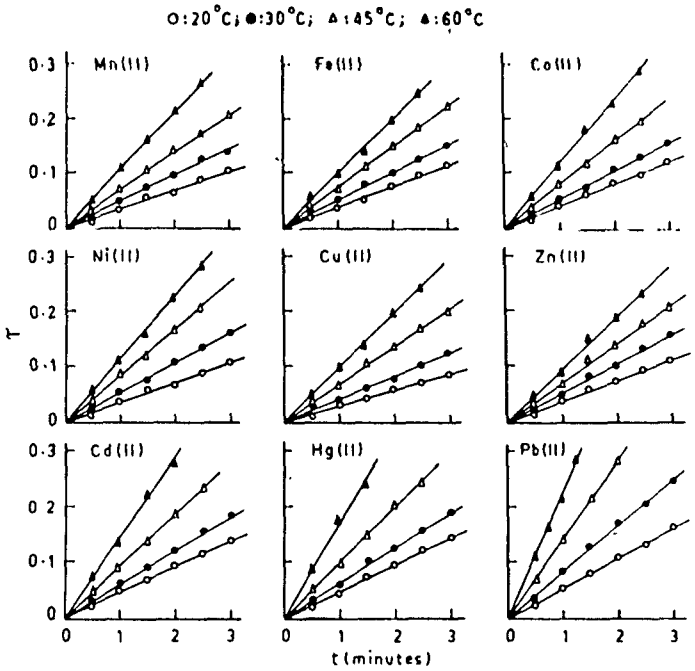


Fig. 6. Plots of τ versus t for different H(I)-heavy metal(II) exchanges at different temperatures on titanium(IV) arsenosilicate under the conditions of particle diffusion.

TABLE 6

Slopes of τ versus t plots at different temperatures

Migrating ion	S (s^{-1}) $\times 10^4$			
	20°C	30°C	45°C	60 C
Mn(II)	5.450	7.850	11.36	17.44
Fe(III)	6.333	8.330	12.40	16.67
Co(II)	6.667	8.511	13.33	19.44
Ni(II)	5.925	8.914	13.89	18.88
Cu(II)	4.666	6.790	11.21	16.30
Zn(II)	6.000	8.510	11.43	15.36
Cd(II)	7.658	10.000	15.67	24.17
Hg(II)	7.801	10.33	16.67	28.10
Pb(II)	8.915	13.81	23.75	37.78

versus t plots at different temperatures for the metal ions under study are shown in Fig. 6, while their slopes are given in Table 6.

Particle size affects the rate of exchange considerably. A plot of S versus $1/r_0^2$ (Fig. 7) shows that the rate of exchange is inversely proportional to the

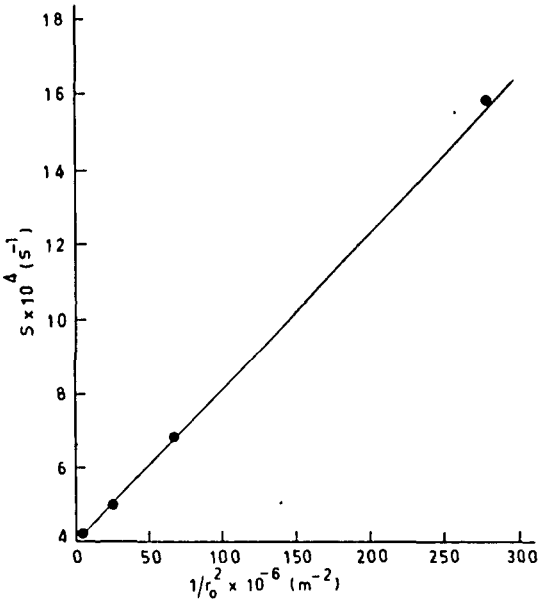


Fig. 7. Plot of S versus $1/r_0^2$ for Cu(II) at 30°C on titanium(IV) arsenosilicate.

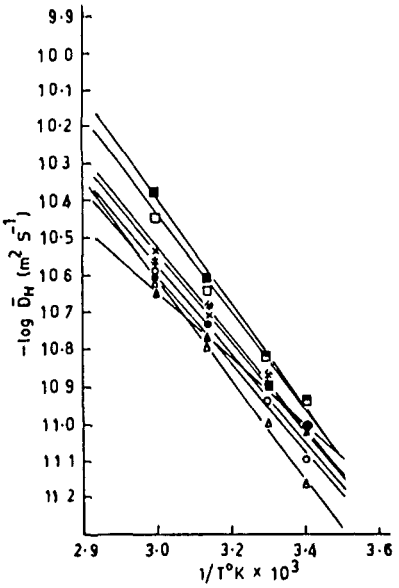


Fig. 8. Plots of $-\log \bar{D}_{11}$ versus $1/T$ (K) for (○) Mn(II); (●) Fe(II); (×) Co(II); (×) Ni(II); (△) Cu(II); (▲) Zn(II); (□) Cd(II); (■) Hg(II).

particle size squared which is a fundamental condition for a particle -diffusion-controlled phenomenon.

The S values are related to $\bar{D}_{11}$ as follows:

TABLE 7

D_0, E_a and ΔS^* values for the exchange of H(I) with some heavy metal ions on titanium(IV) arsenosilicate

Metal ion exchanging with H(I)	Ionic radius (Å)	Ionic mobility ($cm^2 V^{-1} s^{-1}$)	D_0 ($m^2 s^{-1}$)	E_a ($kJ\ mol^{-1}$)	ΔS^* ($J\ deg^{-1}\ mol^{-1}$)
Mn(II)	0.91	0.00028	8.91×10^{-8}	22.63	−31.35
Fe(II)	0.83	0.00045	1.01×10^{-7}	22.76	−30.29
Co(II)	0.82	0.00043	1.22×10^{-7}	23.07	−28.76
Ni(II)	0.78	0.00044	1.41×10^{-7}	23.36	−27.52
Cu(II)	0.70	0.00046	2.75×10^{-7}	25.77	−21.97
Zn(II)	0.83	0.00047	1.10×10^{-8}	17.09	−48.77
Cd(II)	1.03	0.00046	3.39×10^{-7}	25.24	−20.24
Hg(II)	1.12	–	6.46×10^{-7}	26.76	−14.88
Pb(II)	1.32	0.00061	2.88×10^{-6}	29.95	−2.439

$$S=\frac{\bar{D}_H}{r_0^2}$$

The values of $-\log \bar{D}_H$ obtained using this equation were plotted against $1/T$. Straight lines are obtained for all the metal ions studied as shown in Fig. 8, justifying the validity of the Arrhenius equation

$$\bar{D}_H = D_0 \exp(-E_a/RT)$$

The pre-exponential constants D_0 are obtained from the intercepts of the lines while the E_a values can be calculated from the slopes of the plots.

The entropy of activation (ΔS^*) was obtained by substituting D_0 into the equation

$$D_0 = 2.72 d^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right)$$

where k and h are Boltzmann and Planck constants, d is the ionic jump distance [11] at 0.5 nm, R is the gas constant and T is 273 K.

The values of the diffusion coefficient, D_0, energy of activation, E_a, and entropy of activation, ΔS^*, thus obtained, are summarized in Table 7. It is evident from this table that ΔS^* is highest for the H(I)–Pb(II) exchange. This is perhaps due to the highest mobility of Pb(II) (60.8) among the metal ions studied, as supported by the finding of the highest selectivity of the exchanger for this metal ion.

ACKNOWLEDGEMENTS

The authors thank Professor A.U. Malik for the research facilities and the C.S.I.R., India for the financial assistance.

REFERENCES

1 K.G. Varshney, S. Agrawal and K. Varshney, Sep. Sci. Technol , 18 (1983) 59.
2 K.G. Varshney, S. Agrawal and K. Varshney, J. Liq. Chromatogr., 6 (1983) 1535.
3 K.G. Varshney, S. Agrawal and K. Varshney, Anal. Lett., 16 (1983) 685.
4 K.G. Varshney, S. Agrawal, K. Varshney and V. Saxena, Anal. Lett., 17 (1984) 2111.
5 F.D. Snell and C.T. Snell, Colorimetric Methods of Analysis, Vol. 2, 3rd edn, Van Nostrand, Princeton, NJ, 1959, p. 438.
6 E.B. Sandell, Colorimetric Determination of Traces of Metals, Vol. 3, Interscience, New York, 1959, p. 282.
7 F.D. Snell and C.T. Snell, Colorimetric Methods of Analysis, Vol. 2, Van Nostrand, Princeton, NJ, 1959, p. 695.
8 N.H. Furman, Standard Methods of Chemical Analysis, Vol. 1, 6th edn, Van Nostrand, Princeton, NJ, 1963.
9 A.I. Vogel, Textbook of Quantitative Inorganic Analysis, 4th rev. edn, Clay (The Chaucer Press), Hungary, 1978.
10 M.L. Berardilli, P.C. Galli, A. LaGinestra, M.A. Massucci and K.G. Varshney, J. Chem. Soc. Dalton Trans., (1985) 1737.
11 R.M. Barrer, R.F. Bartholomew and L.V.C. Rees, J. Phys. Chem. Solids, 12 (1961) 21.

Colloids and Surfaces, 36 (1989)405-416
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

2·19

Synthesis, Ion Exchange Behaviour and Characterization of Chromium(III) Arsenosilicate Cation Exchanger

K.G. VARSHNEY, A.A. KHAN and M.S. SIDDIQUI

Applied Chemistry Department, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002 (India)

(Received 4 August 1988; accepted 7 December 1988)

ABSTRACT

Chromium(III) arsenosilicate, a new cation exchanger has been synthesized. Its characterization has been made using X-ray, IR and TGA methods. The chemical composition, ion exchange capacity, elution curve, concentration curve, pH titrations and distribution studies have also been done in order to establish its chemical behaviour as an ion exchanger.

INTRODUCTION

Inorganic ion exchangers based on metals like zirconium, titanium, hafnium, etc. have a major disadvantage in that they are expensive compared to organic resins. Thus, cost outweighs the advantage of simplicity of inorganic synthesis as against the organic one. Chromium(III) and iron(III) salts should, therefore, be preferred if they give satisfactory ion exchange properties. Ferric phosphate and chromium(III) arsenophosphate prepared earlier have shown promising ion exchange behaviour [1,2]. Chromium(III) arsenosilicate has been selected in the present study in order to study its ion exchange characteristics in relation to other materials of this class. Its synthesis, characterization and ion exchange behaviour are discussed in this paper.

EXPERIMENTAL

Reagents and chemicals

Chromium(III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) and sodium meta-silicate ($Na_2SiO_3 \cdot 5H_2O$) used in these studies were from BDH (Poole, U.K.) while disodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was of Analar grade (98.5–

0166-6622/89/$03.50

TABLE 1

Instruments used for the various studies

Studies made	Instrument used and its model
pH measurements	pH meter, Model LI-10 Elico (India)
Infrared spectroscopy	Beckman IR-20 spectrometer
Atomic absorption spectroscopy	Pye Unicam Model Sp-2900
X-ray diffraction	Philips X-ray diffraction unit with a Mo-K_α target
Thermogravimetry	Perkin-Elmer TGS-1[a]

[a]Heating rate, 8°C min^{-1}; chart speed, 20 cm h^{-1}; holder, platinum; sensitivity, 100 μV; atmosphere, static air; reference, alumina; initial weight of the sample, 14.0 mg; weight of the residue, 9.9 mg.

TABLE 2

Synthesis of various samples of chromium(III) arsenosilicate as a cation exchanger

Sample No	Concentration of mixing solutions (M)			Mixing ratio	Na^+-ion exchange capacity
	Cr	As	Si	Cr:As:Si	(meq dry g^{-1})
A-1	0.05	0.05	0.05	1:1:1	0.24
A-2	0.05	0.05	0.05	1:1:2	0.30
A-3	0.1	0.1	0.1	2:1:1	0.74
A-4	0.1	0.1	0.1	3:1:1	0.41
A-5	0.1	0.1	0.1	3:2:2	0.36

99%) obtained from Merck (Darmstadt, F.R.G.). Other reagents and chemicals were also of high purity grade.

Instruments used for the various studies are given in Table 1.

Preparation of the reagent solutions

Stock solutions (1.0 M) of chromium(III) nitrate, disodium hydrogen arsenate and sodium meta-silicate were prepared in demineralized water (DMW). Further dilutions of the desired concentrations were also made with DMW.

Synthesis of the ion exchange material

A number of samples of chromium(III) arsenosilicate were prepared by mixing the solutions of chromium(III) nitrate, disodium hydrogen arsenate and sodium meta-silicate in different volume and concentration ratios as given in Table 2. The pH of the resulting gel was fixed in the range 0–2 by adding nitric

acid with constant stirring. The gel thus obtained was kept for 24 hours at room temperature (~30°C) and filtered by suction. The excess acid was removed by washing with DMW till the pH of the washings was ~6 before drying in an oven at 40°C. The dried gel was then put in DMW to obtain granules of uniform size suitable for column operations. They were converted into the H^+-form by treating with 1 *M* HNO_3 for 24 hours with occasional shaking, intermittently replacing the supernatant liquid with fresh acid. The material obtained was finally washed to pH ~6 and then dried at 45°C. On the basis of its Na^+-ion exchange capacity, appearance and apparent stability in acids and bases, sample A-3 was selected for all studies. The reproducibility was checked by preparing the samples several times following the same procedure and determining the ion exchange capacity of the material every time which varied negligibly (<2%).

Ion exchange capacity

The ion exchange capacity (i.e.c.) was determined by column process. One gram of the exchanger (H^+-form) of uniform mesh size (50–100) was placed in a glass tube having an internal diameter ~1 cm and fitted with glass wool at the bottom. The column length was approximately 1.5 cm. 250 ml of 1 *M* $NaNO_3$ solution was passed through it maintaining a very slow flow rate (~0.5 ml min^{-1}) and the effluent was titrated against a standard (0.1 *M*) NaOH solution. The Na^+-ion exchange capacities of the various samples in terms of the milli-equivalent per dry gram are shown in Table 2. The gel was also refluxed in the mother liquor for 48 hours in an attempt to obtain crystalline or semi-crystalline material. However, this treatment reduced the i.e.c. to almost zero.

Thermal stability

Several 1 g portions of the sample (A-3) were heated at various temperatures in a muffle furnace for one hour each and the i.e.c. was determined as above by the column process after cooling them to room temperature. The results are shown in Table 3.

Effect of eluant concentration on the ion exchange capacity

250 ml portions of $NaNO_3$ solutions of varying concentrations (0.2, 0.5, 0.8, 1.0, 1.2 *M*) were passed through several columns each containing one gram of the exchanger in the H^+-form with a flow rate 0.5 ml min^{-1}. The H^+ ions thus eluted out were titrated against a standard (0.1 *M*) NaOH solution. A maximum elution was observed with concentrations 1 *M* and above of $NaNO_3$ solution.

TABLE 3

Ion exchange capacity and appearance of chromium(III) arsenosilicate after heating to various temperatures for one hour

Heating temperature (°C)	Na^+-ion exchange capacity (meq dry g^{-1})	Appearance
45	0.74	Dark green
100	0.74	Dark green
200	0.46	Dark green
300	0.32	Dull green
400	0.11	Light black
600	0.00	Dark black
800	0.00	Dark black

Elution behaviour

The column containing one gram of the material in the H^+ form was eluted with 1 *M* $NaNO_3$ solution (250 ml) having a standard flow rate as above and 10 ml fractions of the effluent were collected. They were titrated for the H^+ ions released against a standard NaOH solution. Figure 1 shows a total release of the H^+ ions in 250 ml of the effluent.

Ion exchange capacity for different metal ions

Ion exchange capacity of the material was also determined by passing different metal ion solutions through the exchanger column in the H^+-form by the method described above. The results are shown in Table 4.

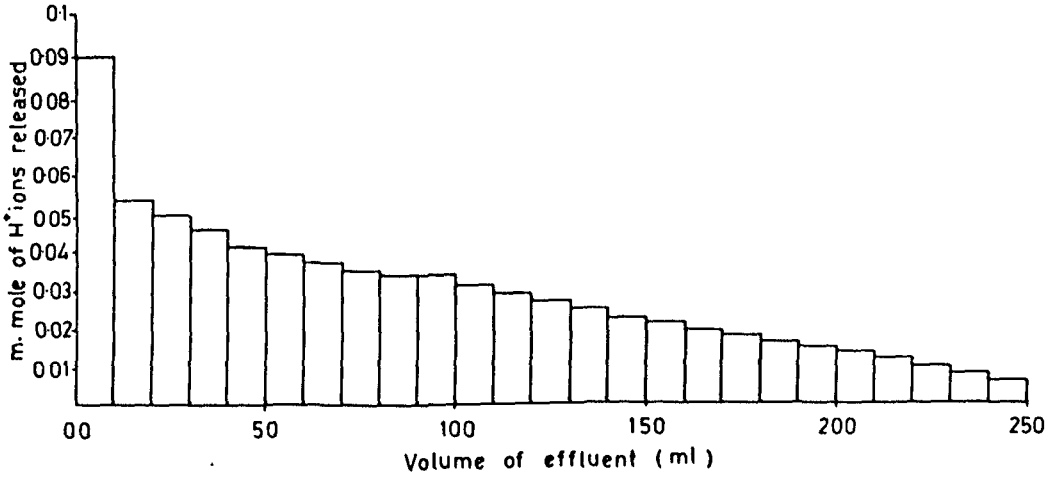


Fig. 1. Histograms showing the elution behaviour of chromium(III) arsenosilicate cation exchanger.

TABLE 4

Ion exchange capacity of chromium(III) arsenosilicate for various metal solutions

Metal solutions	Ion exchange capacity (meq dry g^{-1})
LiCl	0.51
$NaNO_3$	0.74
KCl	0.86
$Ca(NO_3)_2$	0.32
$Sr(NO_3)_2$	0.42

pH Titrations

pH Titrations performed by the batch process using the method of Topp and Pepper [3]. 500 mg portions of the exchanger in the H^+-form were placed in each of several 250 ml conical flasks, followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml, to keep the ionic strength constant (0.15 *M*). The pH of the solution was recorded after 24 hours with intermittant shaking and plotted against the milli-equivalents of the OH^- ions added. The results are shown in Fig. 2.

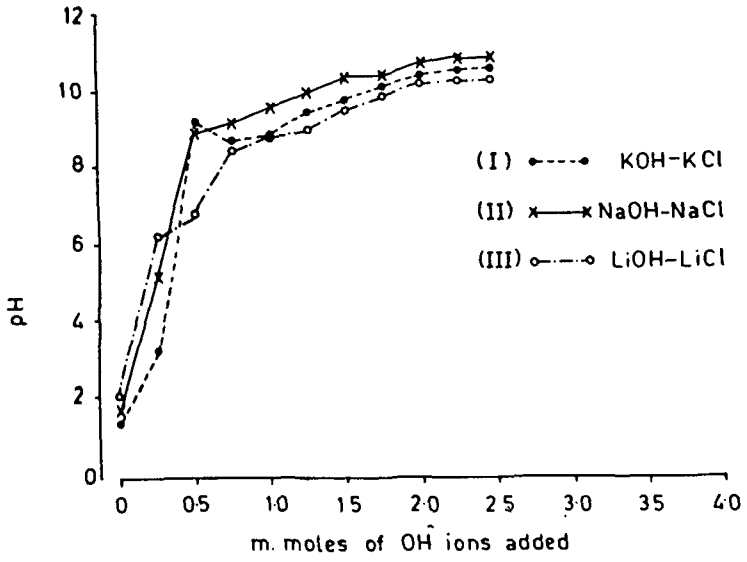


Fig. 2. pH Titration curve for chromium(III) arsenosilicate cation exchanger in various alkali metal hydroxides.

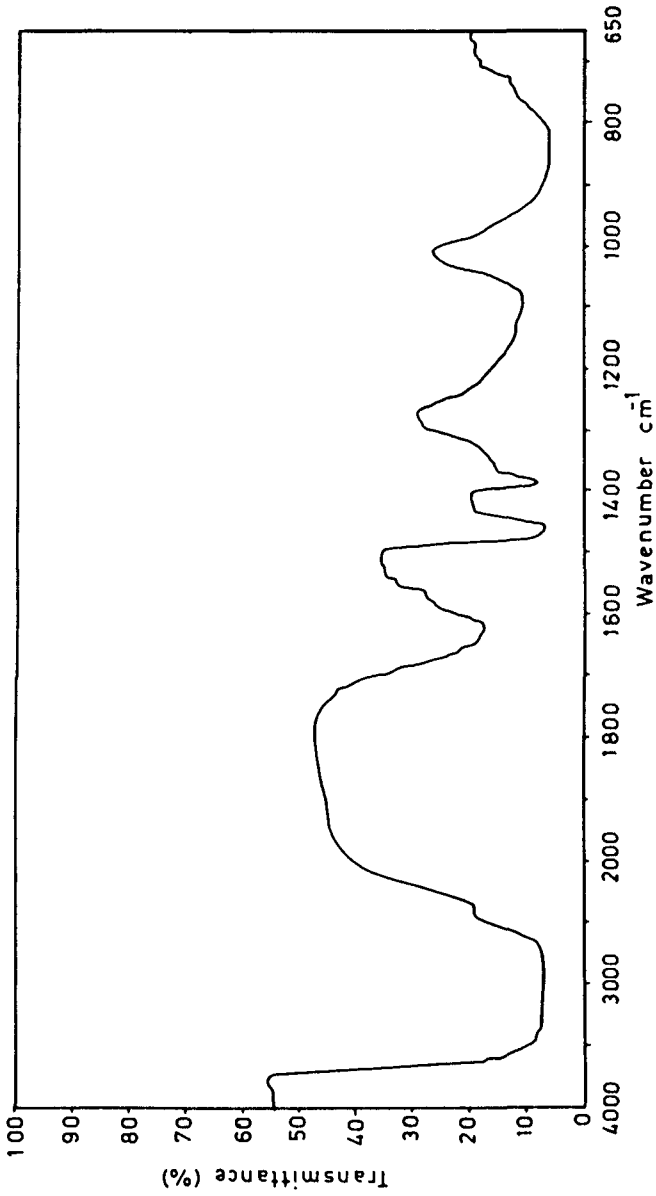


Fig. 3. Infrared spectra of chromium(III) arsenosilicate in H^+-form.

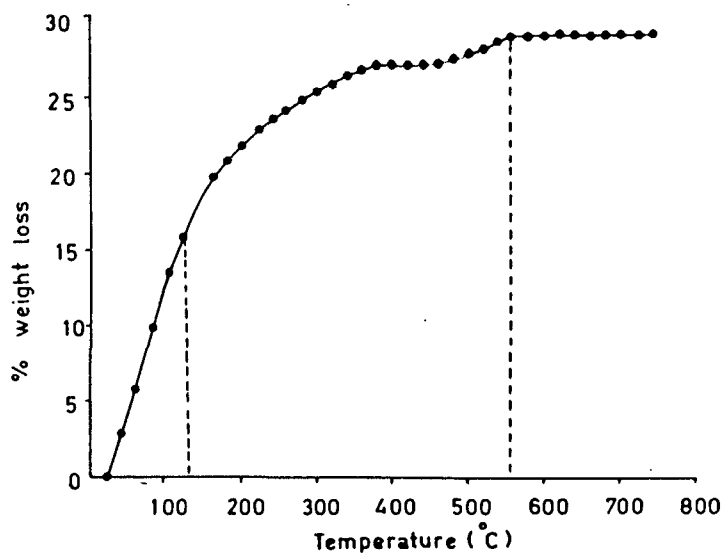


Fig. 4. TGA curve for chromium(III) arsenosilicate in H^+-form.

IR and X-ray studies

The IR spectra of chromium(III) arsenosilicate in H^+-form taken by the KBr disc method at room temperature are shown in Fig. 3. The X-ray diffractogram indicates the amorphous nature of the material.

Thermogravimetric analysis

Figure 4 shows the percent weight loss that occurred in the sample on heating up to 780°C (TGA curve), while Fig. 5 illustrates the DTA and DTG curves for the same sample.

Composition

Chromium and arsenic were determined in the sample by atomic absorption spectrophotometry. Silicon was determined by gravimetry [4] as follows.

250 mg of the powdered exchanger were fused with ~4 g of Na_2CO_3 in a platinum crucible and transferred into a 75 ml solution of 4 *M* HCl. The volume was reduced by ~50% by evaporation. Then the solution was put in a desiccator to cool and to avoid undue exposure to atmospheric contamination. The undissociated silica was filtered through a Whatman No 41 paper and washed with 4 *M* HCl. The decomposed sample was heated to dryness to separate the silica as insoluble $SiO_2 \cdot xH_2O$. The two washed precipitates containing all the silica present in the sample were ignited in a platinum crucible to silicon diox-

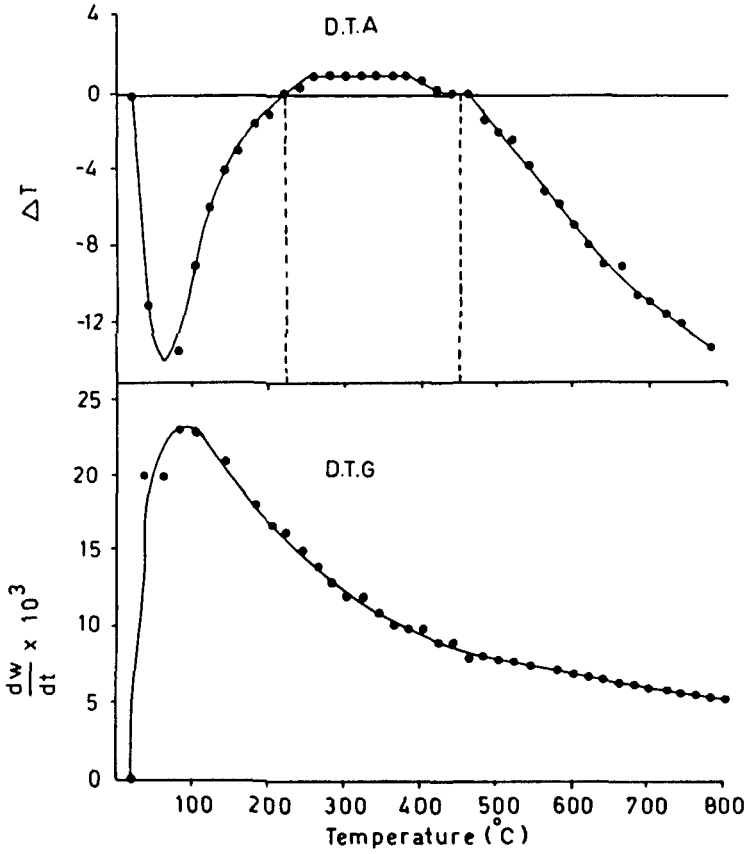


Fig. 5. DTA and DTG curves for chromium(III) arsenosilicate in H$^+$-form.

ide and weighed. The average percentage of silica in the exchanger on the basis of six determinations was 8.07.

Based on the composition studies of the exchanger the Cr(III), As(V) and Si(IV) were found to be in a molar ratio 4:5:3.

Distribution studies

250 mg portions of the exchanger in the H^+-form were shaken at $30 \pm 2°C$ for 4 hours in 25 ml of the metal solution in different media, adjusting the initial metal ion concentration by less than 3% of the total capacity of the ion exchanger. The metal ions in the solutions before and after equilibrium were determined by EDTA [5] and the distribution coefficients (K_d) were determined using the formula:

TABLE 5

K_d values of metal ions on chromium(III) arsenosilicate in DMW, perchloric acid and nitric acid media

Metal ion	K_d values				
	DMW	0.01 *M* $HClO_4$	0.1 *M* $HClO_4$	0.01 *M* HNO_3	0.1 *M* HNO_3
Mg(II)	2	8	11	8	8
Ca(II)	11	7	30	11	TA
Ba(II)	35	1	14	7	27
Sr(II)	TA[a]	5	9	5	17
Cu(II)	18	0	6	2	2
Fe(III)	125	42	42	80	12
Cd(II)	0	0	0	0	0
Co(II)	4	80	TA	8	TA
Mn(II)	7	0	151	0	13
Zn(II)	36	0	0	13	88
Al(III)	120	812	120	812	17
Ni(II)	5	2	TA	14	249

[a]TA = total adsorption.

TABLE 6

K_d values of metal ions on chromium(III) arsenosilicate in acetic acid, tartaric acid, nicotine and pyridine media

Metal ion	K_d values					
	0.01 *M* CH_3COOH	0.1 *M* CH_3COOH	0.01 *M* $(CHOH\,COOH)_2$	0.1 *M* $(CHOH\,COOH)_2$	1% Nicotine	1% Pyridine
Mg(II)	8	8	12	12	TA[a]	74
Ca(II)	4	5	0	16	TA	TA
Ba(II)	21	1	1	1	TA	TA
Sr(II)	5	10	17	770	TA	TA
Cu(II)	1	7	7	24	TA	1800
Fe(III)	288	125	28	12	62	TA
Cd(II)	0	13	13	0	107	144
Co(II)	0	0	9	53	377	720
Mn(II)	11	0	128	3	128	TA
Zn(II)	0	0	0	54	88	TA
Al(III)	370	640	208	58	TA	813
Ni(II)	12	3	2	5	495	TA

[a]TA = total adsorption.

$$K_d = \frac{I-F}{F} \cdot \frac{V}{M}$$

where I is the initial volume of the EDTA used, F is the final volume of the EDTA used, V is the total volume of the solution (ml) and M is the mass of the exchanger (g). The K_d values for 12 metal ions in the different solvents used are summarized in Tables 5 and 6.

DISCUSSION

Chromium(III) arsenosilicate prepared during these studies has a Na^+-ion exchange capacity ~ 0.75 meq g^{-1} which is less than the chromium(III) arsenophosphate prepared earlier [2] in these laboratories. It may be due to the difference in the K_a values of silicic and phosphoric acids [6]. Silicic acid being weaker ($K_1 = 1.3 \cdot 10^{-11}$, $K_2 = 1.6 \cdot 10^{-12}$, $K_3 = 2.0 \cdot 10^{-14}$) than phosphoric acid ($K_1 = 7.6 \cdot 10^{-3}$, $K_2 = 6.2 \cdot 10^{-8}$, $K_3 = 4.2 \cdot 10^{-13}$) should be less protogenic and its H^+-ion releasing capacity should be less, thus resulting in weaker acid sites in the exchanger. However, the presence of silicate enhances the stability of the material and hence the disadvantage of an inferior ion exchange capacity is somewhat compensated for.

Composition studies indicate the mole ratio of Cr, As and Si in the material as 4:5:3 which points to the following structure:

$[2\ Cr_2O_3 \cdot 2.5\ As_2O_5 \cdot 3\ SiO_2 \cdot nH_2O]$

The TGA curve (Fig. 4) shows a sharp loss of weight up to $\sim 150°C$ which may be due to the removal of external water molecules from the exchanger. A 16% weight loss at this temperature corresponds to approximately 6.5 H_2O molecules per molecule of the exchanger on the basis of the basic unit of the material as shown above. A further weight loss beyond 150°C may be due to the condensation process taking place and seems to be complete at 550°C. This temperature range (150–550°C) also includes the existence range [7] (435–450°C) of the oxide of arsenic. As_2O_5 obtained from $As_2O_5 \cdot \frac{1}{2}H_2O$ at 193°C begins to decompose [8] into As_2O_3 at 246°C. A sharp endothermic peak below 200°C in the DTA curve (Fig. 5) confirms the removal of external water molecules and a broadened exothermic peak in the range 225–450°C is an indication of a slow decomposition process:

$$As_2O_5 \rightleftharpoons As_2O_3 + O_2$$

accompanied by the condensation process involving the removal of the strongly coordinated H_2O molecules within the framework of the exchanger. Beyond 550°C the exchanger remains simply in the oxide form which obviously does not show any ion exchange capacity (Table 3). A sharp decline in the Na^+-ion

exchange capacity on heating the sample up to 200°C confirms the above propositions.

The material appears to have a selective affinity for K^+ ions among the alkali metals as it shows a maximum i.e.c. (0.86) for this ion (Table 4). However, it does not bind Ca^{2+} and Sr^{2+} so strongly which appears to be its peculiar behaviour among the salts of this class which have earlier shown a better selectivity for alkaline earth metals.

The pH titration curves show an inflection at ~0.5 mmoles OH^- ions added for both KOH and NaOH. For LiOH, however, there are two inflections, one at pH 6 and the other at about 8.2. At pH 6 the H^+ ions released are less than the Li^+ uptake compared to the Na^+ and K^+ uptakes. This also explains the discrepancies in the i.e.c. for various alkali metal ions studied.

The IR spectrum for chromium(III) arsenosilicate is given in Fig. 3 which shows strong bands at 850, 1100, 1370, 1450, 1600 and 3000 cm^{-1}. Metal-oxygen stretching vibrations are indicated [9] by the band at 850 cm^{-1} while those at 1100, 1370 and 1450 cm^{-1} correspond to the arsenate and silicate groups in the structure [10]. Those at 1600 and 3000 cm^{-1} are due to the presence of water of crystallization [11]. The band at 3000 cm^{-1} is also indicative of the strongly hydrogen bonded OH or extremely strongly coordinated H_2O.

The distribution studies (Table 6) indicate significant adsorption for most of the 12 metal ions studied in nicotine and pyridine systems. This behaviour can be useful for some separations such as Fe(III) from Mg(II), Ca(II), Ba(II), Sr(II), Cu(II), Al(III) in nicotine systems, and Mg(II) from Ca(II), Ba(II), Sr(II), Mn(II), Zn(II), Ni(II) and Fe(III) in pyridine systems.

CONCLUSION

The inorganic ion exchanger, chromium(III) arsenosilicate prepared in these studies has shown an exceptionally high selectivity for some metal ions in nicotine and pyridine solutions. The exchanger shows a total adsorption for Mg(II), Ca(II), Ba(II), Sr(II), Cu(II) and Al(III) in nicotine and for Ca(II), Ba(II), Sr(II), Fe(III), Mn(II), Zn(II) and Ni(II) ions in pyridine. On this basis a number of useful separations have been achieved in these two solvent systems.

ACKNOWLEDGMENTS

The authors thank Professor K.T. Nasim for research facilities and the U.P. Council of Science & Technology for the financial assistance to one of them (M.S.S.).

REFERENCES

1 J.P. Rawat and P.S. Thind, Can. J. Chem., 54 (1976) 1892.
2 K.G. Varshney and A.A. Khan, J. Inorg. Nucl. Chem., 41 (1979) 241.
3 N.E. Topp and K.W. Pepper, J. Chem. Soc., (1949) 3299.
4 I.M. Kolthoff and E.B. Sandell, Text Book of Quantitative Inorganic Analysis, Macmillan, New York, 1938, p. 383.
5 C.N. Reilley, R.W. Schmidt and F.S. Sadek, J. Chem. Ed., 36 (1959) 555.
6 Ju. Lurie, Handbook of Analytical Chemistry, Mir, Moscow, 1975, pp. 279-280.
7 H. Backstrom, Z. Anal. Chem., 31 (1892) 663.
8 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1953, p. 297.
9 C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963, p. 338.
10 Ibid., p. 354.
11 Ibid., p. 359.

J. Indian Chem. Soc.,
Vol. LXI, March 1984, pp. 220-224

2.20 Synthesis and Analytical Applications of Thorium(IV) Phosphosilicate—A New Mercury Selective Cation Exchanger : Effect of Gamma Irradiation on its Ion-Exchange Behaviour

K. G. VARSHNEY, UMA SHARMA and SIMA RANI

Analytical Laboratories, Chemistry Section,
Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202 001

Manuscript received 1 March 1983, revised 18 August 1983, accepted 11 February 1984

A new mercury selective inorganic cation exchanger, thorium(IV) phosphosilicate has been synthesized and studied for its ion-exchange behaviour. The exchanger has been characterized by chemical analysis and infrared spectra, X-ray diffraction, thermogravimetry and *p*H-titration. The effect of gamma irradiation on its ion-exchange behaviour has also been studied. Finally, the utility of the material has been demonstrated by achieving some binary separations of metal ions, and by separating Hg(II) from some synthetic amalgam solutions.

THORIUM phosphate prepared by Alberti and Costantino[1] showed an excellent ion exchange behaviour and was found suitable for preparing support-free inorganic sheets[2,3]. As silicates are generally temperature resistant and stable under chemical attack[4], it is interesting to study a material which consists of both phosphate and silicate groups attached to a metal. Titanium(IV) phosphosilicate[5], for example, has been found useful for the separation of Zr(IV) from Nb(V) and of Pu(IV) from Cs(I). Similarly, phosphosilicates of Zr(IV), Ce(IV) and Sn(IV) have been synthesized[6-9] and their ion-exchange properties studied. The present paper reports a systematic study on the synthesis and properties of a new mercury selective thorium(IV) phosphosilicate (TPS) cation exchanger. The exchanger has also been utilized for the column separation of metal ions from some binary mixtures and of mercury(II) from some synthetic amalgam solutions.

Experimental

Thorium nitrate, $Th(NO_3)_4.6H_2O$, and all the acids (phosphoric, nitric, sulphuric, hydrochloric, perchloric and organic) used in this study were obtained from B.D.H., Poole, England. Sodium silicate, $Na_2SiO_3.3H_2O$, used was a Riedel, Germany product. All other reagents and chemicals were of AnalaR grade.

*p*H-measurements were made on an Elico model LI-10, *p*H-meter. IR studies were performed on a Beckman IR-20 spectrophotometer. X-ray studies were made on a Philips X-ray unit using a Mo–Kα target. Thermogravimetry was done on a modern TGA balance of the F. C. I. Ltd., India.

Synthesis of the ion-exchange material :

To a definite volume of aqueous sodium silicate solution (0.1 *M*) was added conc. HCl (5 ml per 100 ml of the solution) followed by a definite volume of thorium nitrate (0.1 *M*) solution. The *p*H of this mixture was adjusted to 9-10 by NaOH and the resultant slurry was allowed to stand overnight. It was then filtered, washed with demineralised water (DMW), and mixed with a fixed volume of the H_3PO_4–HNO_3 mixture (1 *M* in terms of each acid). The gel thus obtained was filtered and washed thoroughly before drying at 45° in an air oven. The dried material was cracked in DMW to form small granules of uneven sizes. Fine particles were removed by decantation and the rest were placed in 1 *M* HNO_3 to convert them into the H^+–form which were finally dried at 45°. Table 1 summarizes the synthesis and Na^+ ion exchange capacity of the various samples prepared. Reproducibility was checked by preparing several samples by the same method and observing their ion-exchange capacity many times. All the studies were performed on the sample TPS-1.

TABLE 1—SYNTHESIS OF SOME SAMPLES OF Th(IV) PHOSPHOSILICATE AND THEIR Na^+ ION-EXCHANGE CAPACITY

Sample	Mixing ratio of the solutions $Th(NO_3)_4$: $Na_2SiO_3.3H_2O$: $(H_3PO_4+HNO_3)$	Na^+–ion exchange capacity (meq/dry g)
TPS-1	1 : 1 : 1	1.66
TPS-2	2 : 1 : 1	1.66
TPS-3	1 : 1 : 2	1.64
TPS-4	1 : 2 : 1	1.66

Ageing effect : The gel was kept for different time intervals before filtering. After processing as above, their ion-exchange capacity was determined as usual. The results are summarized in Table 2.

TABLE 2—EFFECT OF AGEING ON THE ION EXCHANGE CAPACITY OF Th(IV) PHOSPHOSILICATE (TPS-1)

Ageing time (hr)	Na^+ – ion exchange capacity (meq/g)
24	1.66
48	1.68
72	1.74
120	1.78
240	1.82
500	1.91
480	1.98

Composition of the material : A weighed amount (500 mg) of the powdered exchanger was dissolved in conc. hydrochloric acid (10 ml) by heating. After dilution to ~100 ml with water, thorium was precipitated[10], filtered, ignited and weighed as ThO_2. Phosphorous was determined as phosphate by back titration with EDTA[11] and silica was determined as SiO_2[12]. The results are summarized in Table 3 which are the mean of atleast five observations

TABLE 3—COMPOSITION OF Th(IV) PHOSPHOSILICATE

Sample	Millimoles of components per 500 mg of the exchanger			
	Thorium	Phosphorous	Silicon	Mole ratio Th : P : Si
TPS-1	1.39	1.78	1.56	1 : 1.28 : 1.12
TPS-2	1.38	1.44	2.12	1 : 1.04 : 1.53
TPS-3	1.42	1.56	1.84	1 : 1.09 : 1.29
TPS-4	1.64	1.36	1.68	1 : 0.82 : 1.02

Ion-exchange capacity (iec) : This was determined as usual by the column process[13]. The values in meq/g (dry) for different metals are Li(I) (0.98), Na(I) (1.66), K(I) (1.68), NH_4(I) (0.82), Mg(II) (1.54), Ba(II) (0.96), Ca(II) (1.11). The Na^+ iec of the irradiated samples (1×10^6, 2×10^6 and 3×10^6 rads) were found to be 1.44, 1.34 and 1.21 meq/g, respectively.

Elution behaviour : The optimum concentration of $NaNO_3$ for the complete elution of hydrogen ions in a fixed volume (125 ml) from the exchanger was found to be 1 *M*. The elution curve was then drawn by taking this concentration of the eluant and is shown in Fig. 1.

Irradiation effect : Different samples of thorium(IV) phosphosilicate (TPS-1) were irradiated by γ-rays obtained from a ^{60}Co source under a dose rate of 0.4 *M* rads/hr, the total doses being 1×10^6, 2×10^6 and 3×10^6 rads, respectively using $FeSO_4$ as the dosimeter. The ion-exchange behaviour of these irradiated samples was studied as mentioned above.

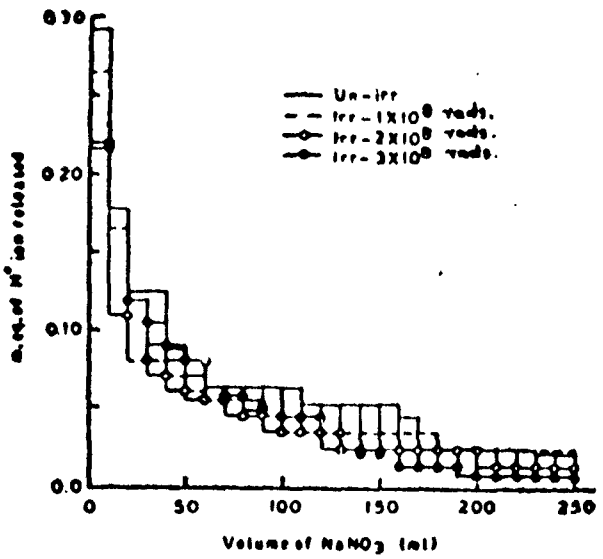


Fig. 1. Elution behaviour of Th(IV) phosphosilicate (TPS-1).

Thermal stability : Several samples were heated at different temperatures for 1 hr each and the iec was determined as above after cooling them to room temperature. It was observed that the material retains about 80% of its iec at 200° beyond which it loses it very sharply.

Chemical stability : 250 mg of the material was placed in 25 ml solution of an acid or a base and shaken intermittently for 24 hr. The solution was then analyzed for dissolved thorium[14], phosphorous[15] and silica[16] contents using standard spectrophotometric methods. The results are shown in Table 4.

TABLE 4—SOLUBILITY OF THORIUM(IV) PHOSPHOSILICATE (TPS-1) IN VARIOUS SOLVENT

Solution 25 ml	Amount dissolved in mg/25 ml of the exchanger		
	Th	P	Si
1 *M* HNO_3	1.5	0.0	1.8
2 *M* HNO_3	3.0	1.8	3.8
1 *M* $HClO_4$	2.8	0.0	3.4
2 *M* $HClO_4$	3.2	0.0	6.3
2 *M* HCl	3.5	1.4	6.3
1 *M* H_2SO_4	6.3	3.0	6.8
1 *M* CH_3COOH	2.5	1.4	1.5
1 *M* KNO	0.0	1.5	0.0
1 *M* $NaNO_3$	1.3	0.0	0.0
1 *M* NH_4NO_3	1.3	0.0	1.5
0.05 *M* NaOH	3.0	2.5	6.8
0.1 *M* NaOH	3.0	3.9	6.8
0.1 *M* KOH	2.8	3.9	2.5

pH-Titrations : 500 mg of the exchanger was taken in each of several 250 ml conical flasks followed by equimolar solutions (0.05 *M*) of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml. The *p*H values recorded after keeping the solutions overnight for equilibrium were plotted against the milliequivalents of OH^- added (Fig. 2). It shows a monofunctional

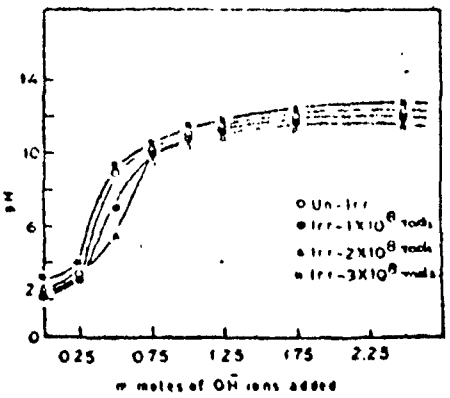


Fig. 2. pH-titration curve for Th(IV) phosphosilicate (TPS-1).

behaviour similar to that of a strong acid cation exchanger.

These studies were performed on sample TPS-1 for different metal ions in various solvents in the following manner.

250 mg exchanger beads in H^+ form were equilibrated with 25 ml of the selected solvent by shaking at room temperature for 4 hr. The exchanger beads were separated by decantation and the solution was analyzed volumetrically for the presence of metal ions, using EDTA as titrant[17]. The initial metal ion concentration was so adjusted that it may not exceed 3% of the total iec of the material. The K_d values, as summarized in Table 5, were then calculated by the formula

$$K_d = \frac{I-F}{F} \times \frac{V}{A} \text{ (ml/g)}$$

where I is the initial volume of EDTA used, F the final volume of EDTA used, V the total volume of the solution, and A the amount of exchanger in g.

Separations achieved : Based on the distribution behaviour, several binary separations were achieved on a column having 2 g of the exchanger in H^+ form, taken in a glass tube having an i.d. ~0.6 cm. The flow rate was maintained at ~0.5 ml/min. Table 6 summarizes the results along with the limits of separation of Hg(II) from Zn(II), Cd(II) and Cu(II). The height equivalent to a theoretical plate (HETP) was also calculated[18] to demonstrate the efficiency of the column, using the formula

$$\text{HETP} = \frac{Lb^2}{8V^2_{max}}$$

where L is the column height (7.5 cm), b the peak width (ml) at a height of 0.368 C_{max} and V_{max} the eluant volume (ml) at peak.

Results and Discussion

Thorium(IV) phosphosilicate thus turns out to be a selective cation exchanger for Hg(II). It can be used effectively for column chromatographic separation of Hg(II) from other metal ions, as Table 6 shows. Mercury has also been separated from some synthetic alloys (amalgams) such as Zn(II)-Hg(II), Cd(II)-Hg(II), Cu(II)-Hg(II), Mn(II)-Hg(II) and Ni(II)-Hg(II), the upper limit of separation being 401.18 μg Hg(II) per 2 g of the column. Thus, the material appears to have a potential application in analytical field. The advantage of the method lies in its simplicity and versatility. The iec of the material increases on ageing the gel formed after mixing the component solutions (Table 2) which is obvious because of the equilibrium attained by the system with time. The material shows a monofunctional behaviour (Fig. 2) which may be due to similar pK_a values[19] of the two acid groups present in it.

The thermogravimetric analysis (Fig. 3) shows the first inflexion point at 160°, corresponding to a weight loss of ~20%, which may be due to the removal of external water molecules from the gel.

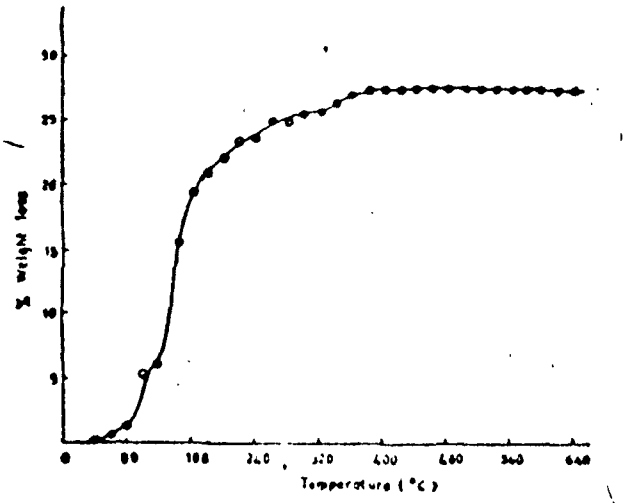


Fig. 3. Thermogram of Th(IV) phosphosilicate (TPS-1).

After this temperature the loss rate is considerably slowed down probably because of the condensation process which continues upto ~400°, the total loss at that temperature being ~25%. The composition studies also indicate nearly the same amount of water content in the material thus confirming the TGA results. On the basis of chemical analysis, ir and TGA studies, the formula of this salt may be tentatively suggested as :

$$[ThO_2.H_3PO_4.H_4SiO_4].nH_2O$$

If we assume the weight due to the presence of the external water molecules in the gel as ~20% of the total weight, the number of such moles (n) per mole of the exchanger can be determined on the basis of the Alberti's equation[20]

$$18n = \frac{X(M+18n)}{100}$$

where X is the percent water content and M + 18n the molecular weight of the material. It gives the value of n as 6.3.

TABLE 5—K_d VALUES OF SOME METAL IONS ON THORIUM(IV) PHOSPHOSILICATE (TPS-1)

Sl. No.	Metal Ion	DMW*	0.01 *M* HCl	0.1 *M* HCl	0.01 *M* HNO_3	0.1 *M* HNO_3	0.01 *M* $HClO_4$	0.1 *M* $HClO_4$	0.01 *M* CH_3COOH	0.1 *M* CH_3COOH
1.	Zn(II)	110	80	33	28	10	48	18	40	14
2.	Cd(II)	100	64	25	67	7	51	26	72	12
3.	Hg(II)	1900	1150	1150	1120	1120	1120	1120	1120	1120
4.	Mg(II)	110	86	48	64	18	92	38	92	18
5.	Ca(II)	78	64	26	86	14	56	12	46	16
6.	Sr(II)	160	102	86	78	42	110	84	94	66
7.	Ba(II)	800	586	410	778	542	568	898	586	420
8.	Mn(II)	80	28	0	16	12	42	8	32	12
9.	Fe(III)	900	61	0	78	0	0	0	0	0
10.	Co(II)	975	690	486	616	79	616	79	616	79
11.	Ni(II)	75	0	0	38	0	0	0	0	0
12.	Cu(II)	45	15	8	17	1	98	22	16	0
13.	Pb(II)	925	441	180	598	158	426	128	778	295
14.	Al(III)	98	0	0	0	0	5	0	5	0

*Demineralised water.

TABLE 6– SALIENT FEATURES OF SOME SEPARATIONS ACHIEVED ON THORIUM(IV) PHOSPHOSILICATE (TPS-1) COLUMNS

Sl. No.	Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Limit of loading in μg on 1 g exchanger	Eluent used (ml)	HETP (cm)
1.	Zn(II)-Hg(II)	254.9 Zn	254.9 Zn	0	50-300	0.01 *M* HNO_3, (40)	1.85
		581.7 Hg	581.7 Hg	0	40-850	1 *M* HNO_3, (50)	—
2.	Cd(II)-Hg(II)	168.6 Cd	168.6 Cd	0	65-400	0.01 *M* HNO_3, (20)	1.84
		401.2 Hg	401.2 Hg	0	40-590	1 *M* HNO_3, (40)	—
3.	Cu(II)-Hg(II)	197.0 Cu	197.0 Cu	0	68-250	0.01 *M* HNO_3, (80)	2.4
		481.2 Hg	401.2 Hg	−4.8	40-590	1 *M* HNO_3, (40)	—
4.	Cu(II)-Pb(II)	198 Cu	192 Cu	−2	20-400	0.01 *M* HCl, (40)	7.4
		310 Pb	290 Pb	−6.4	150-550	0.1 *M* HCl, (30)	—
5.	Cu(II)-Co(II)	287 Cu	287 Cu	0	100-650	0.1 *M* HCl, (30)	6.54
		232 Co	219 Co	−5.6	65-480	1 *M* HCl, (30)	—
6.	Ni(II)-Co(II)	163 Ni	159 Ni	−2.45	60-400	0.1 *M* HNO_3, (40)	1.84
		118 Co	95 Co	−11	150-350	1 *M* HNO_3, (40)	—
7.	Mg(II)-Ba(II)	448 Mg	448 Mg	0	30-580	DMW, (40)	1.84
		287 Ba	299 Ba	−8.3	40-600	0.1 *M* HCl, (30)	—
8.	Ca(II)-Ba(II)	448 Ca	448 Ca	0	24-800	DMW, (60)	2.4
		524 Ba	524 Ba	0	40-800	0.1 *M* HCl, (20)	—

The ir spectrum of this material (Fig. 4) shows several peaks. The broad bands at 600 cm^{-1} is due to polymerization through metal-oxygen linkages and are expected to impart ion exchange properties. The sharp peaks at 750 and 1050 cm^{-1} are due to the presence of the silicate and phosphate groups[21], respectively, while those at 1600 and 3200 cm^{-1} represent the "interstitial" and "external" water molecules. The ir spectra of the irradiated samples (Fig. 4) are essentially similar to that of the normal sample, indicating that the material is generally unaffected by the γ-irradiation upto a total dose of 3×10^6 rads. The iec and elution behaviour are however slightly affected by this treatment as is indicated in Figs. 1 and 2. This study, therefore, clearly illustrates the advantage of using thorium(IV) phosphosilicate under the environment of strong radiations in which the organic resins[22] start decomposing even much below the range studied here.

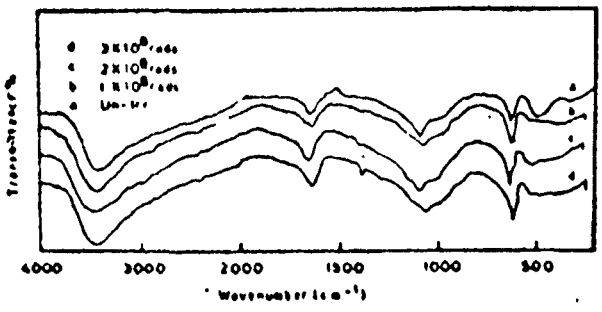


Fig. 4. IR spectra of Th(IV) phosphosilicate (TPS-1).

The distribution studies (Table 5) indicate that, in general, with the increase of the H^+ ion concentration, the K_d values decrease, which is an obvious phenomenon. However, the decrease is not linear with the *p*H, which may be due to the adsorption process, in addition to the pure ion exchange phenomenon taking place on the surface of an inorganic ion exchanger. A definite view in this regard cannot be taken at the moment because of the lack of a thorough study of the distribution behaviour on this material. Such studies are in progress. The most striking feature of the study, however, is the fact that the material is highly selective for Hg(II) in all the systems studied even at low *p*H.

Acknowledgement

The authors thank Prof. M. Qureshi for facilities and the C.S.I.R., New Delhi for financial assistance. Gamma irradiation studies were performed at the Bhabha Atomic Research Centre, Bombay and at the University of Poona, which is gratefully acknowledged.

References

1. G. Alberti and U. Costantino, *J. Chromatogr.*, 1970, 50, 482.
2. A. K. De and K. Chowdhury, *J. Chromatogr.*, 1974, 63, 101.
3. *G. Alberti and U. Costantino (Comitato Nazionale per Energia Nucleare: (NEN) U. S. 8, 985, 611 (Cl. 162-157R, D21 H6/12), 12 Oct. 1976, Appl. 168091, 15 Jul. 1971, 3 p.*
4. F. A. Cotton, "Advanced Inorganic Chemistry", Wiley Eastern Private Limited, Delhi, 1970, p. 469.
5. S. J. Naqvi, L. Huys and L. H. Baetsle, *J. Inorg. Nuclear Chem.* 1971, 33, 4817.
6. R. M. S. Ramaswamy, B. L. Jangida and M. Sundarrsan, *Proc. Ion-Exchange Symp., Bhavnagar, India*, 1978, 187.
7. S. A. Marei and N. Botros, *Talanta*, 1980, 27, 599.
8. K. G. Varshney and A. Premadas, *J. Liquid Chromatogr.*, 1981, 4, 1245.
9. K. G. Varshney and A. Premadas, *J. Liquid Chromatogr.*, 1981, 4, 915.
10. Vogel's "Text-book of Quantitative Inorganic Analysis", Richard Clay, The Chaucer Press Ltd. (Hungary), IVth Ed., 1978, p. 488.
11. Vogel's "Text-book of Quantitative Inorganic Analysis", Richard Clay, The Chaucer Press Ltd., Hungary, IVth Ed., 1978, p. 885.
12. Vogel's "Text-book of Quantitative Inorganic Analysis", Richard Clay, The Chaucer Press Ltd., Hungary, IVth Ed., 1978, p. 601.
13. K. G. Varshney and A. A. Khan, *Talanta*, 1978, 25, 628.
14. I. M. Kolthoff and R. Belcher, "Volumetric Analysis", Interscience, New York, 1957, Vol. 3, p. 320.
15. N. H. Furman, "Standard Methods of Chemical Analysis", VI Edn., D. Van Nostrand Company, Inc., Princeton, New Jersey, 1963, Vol. 1, p. 117.
16. F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis", III Edn, D. Van Nostrand Company, Inc., *Princeton, New York, 1959, Vol. 2, p. 448.*
17. C. M. Reilly, R. W. Schmid and Fawby, *J. Chem. Educ.*, 1959, 36, 555.
18. P. S. Thind and H. Singh, *J. Indian Chem. Soc.*, 1961, 38, 1187.
19. Ju. Lurie, "Handbook of Analytical Chemistry", Mir Publishers, Moscow, IInd Ed., 1975.
20. G. Alberti, E. Torraca and A. Conte, *J. Inorg. Nuclear Chem.*, 1966, 28, 607.
21. J. A. Gadsden Aric, "Infrared Spectra of Minerals and Related Inorganic Compounds", R. J. Acford Ltd., Sussex, 1975.
22. M. Kubota, Y. Konami, H. Nakamura and H. Amano, *J. Radioanal. Chem.*, 1978, 45, 78.

RADIOCHEM.RADIOANAL.LETTERS 58 /3/ 141-146 /1983/

2.21

ADSORPTION STUDIES OF ALKALI METALS ON VARIOUS INORGANIC ION-EXCHANGE MATERIALS USING RADIOTRACERS

K.G. Varshney, S. Agrawal, K. Varshney, U. Sharma, S. Rani

Analytical Laboratories,
Chemistry Section,
Faculty of Engineering and Technology,
Aligarh Muslim University,
Aligarh-202001, India

Received 20 June 1983
Accepted 27 June 1983

A systematic adsorption study of alkali metals /Na, K, Rb, Cs/ on various inorganic ion-exchange materials in distilled water and $HClO_4$ solutions of varying concentrations has been performed using radiotracers. The lg K_d vs. pH graphs show a linear relation on all the materials for Na/I/ and K/I/ ions. Adsorption of Rb/I/ and Cs/I/ ions, however, shows a slight variation.

INTRODUCTION

The use of radiotracers in chemical analysis is well established in determining the extremely small quantities of substances in a mixture. Inorganic ion-exchangers are well known for the separation of metal ions[1], their use being in the nuclear energy industry[2-5] for the separation

of selected nuclides such as ^{137}Cs, ^{90}Sr from the wastes of reactor fuels. Some materials, prepared in these laboratories[6-9] have shown promising ion-exchange behaviour in addition to their thermal and chemical stability. They have also exhibited high resistance towards gamma radiation. The present paper summarizes our adsorption studies for some metal ions of analytical and radiochemical interest on the materials based on Sn/IV/, Zr/IV/ and Sb/V/, using radiotracers.

EXPERIMENTAL

Reagents and chemicals

All the reagents and chemicals used in this study were of Analar grade obtained either from B.D.H. Poole /England/ or E. Merck /Darmstadt, GFR/.

Radiotracers used

The following nuclides were used as radiotracers, the half-lives are given in parenthesis:

^{24}Na /15 h/, ^{42}K /12.5 h/, ^{86}Rb /18.7 d/ and ^{137}Cs /30.2 y/

Instrumentation

Activity measurements were done in a well-type single channel analyser of Electronic Corporation of India Ltd. using a NaI/Tl/ detector.

Ion-exchange materials used

The following inorganic ion-exchangers were prepared by the methods reported earlier with their ion-exchange capacities shown against them:

1. Silica based Sn/IV/ hexacyanoferrate/II/[6] /SnHF/ /1.10 meq/dry g/.
2. Zirconium/IV/ arsenophosphate[7] /ZAP/ /0.94 meq/dry g/.
3. Zirconium/IV/ arsenosilicate[8] /ZAS/ /1.30 meq/dry g/.
4. Antimony/V/ silicate[9] /SbS/ /1.60 meq/dry g/.

Distribution studies

The distribution coefficients /K_d/ were determined for Na/I/, K/I/, Rb/I/ and Cs/I/ ions by the batch process as follows:

100 mg of the exchanger in H^+ form was taken in a conical flask followed by 20 ml of the solvent, 1 ml of the metal ion solution and 1 ml of the carrier solution. The contents were shaken for 3 h with an electric shaker or allowed to stand overnight for attaining equilibrium. Then 10 ml of the supernatant liquid was withdrawn for activity measurement. The standard radioactivity of the tracer solution being known, the K_d values were calculated by the formula:

$$K_d = \frac{/1-F/}{F} \cdot \frac{V}{M} \text{ ml } g^{-1}$$

where F is the fraction of the activity of tracer in solution at equilibrium, V is the volume of the solution /ml/ and M is the mass of the exchanger /g/.

The K_d values were determined in $HClO_4$ solutions of varying pH /1 to 5/ and demineralized water /DMW/. Fig. 1. shows the variation of K_d values of alkali metals with the pH.

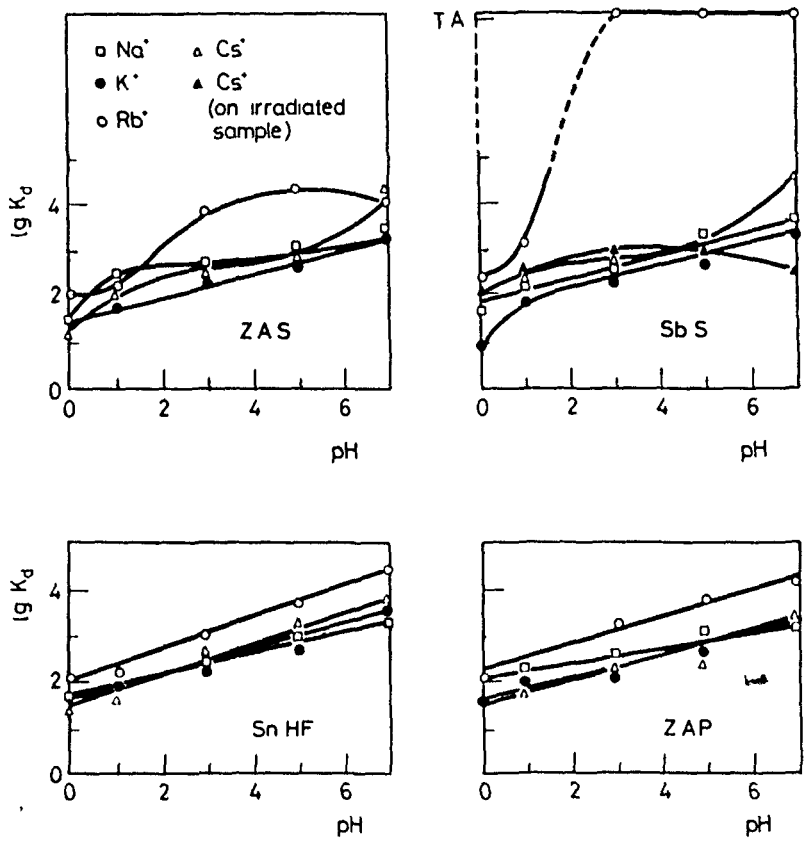


Fig. 1. Effect of pH on the K_d values of alkali metals on various ion-exchangers

DISCUSSION

These studies reveal certain interesting features of inorganic ion-exchangers. SnHF and ZAP show a linear increase in lg K_d values of all the four alkali metals studied against pH /Fig. 1./, the maximum adsorption being for Rb/I/. The slopes of these straight lines are found to be in the following order:

Na/I/ /0.24/ < K/I/ /0.28/ < Cs/I/ /0.32/ < Rb/I/ /0.35/ on SnHF and
Na/I/ /0.17/ < K/I/ /0.23/ < Cs/I/ /0.27/ < Rb/I/ /0.28/ on ZAP.

However, a little deviation from this behaviour is observed on ZAS and SbS ion-exchangers. Although Na/I/ and K/I/ show a linear increase in the lg K_d values against pH, it is not true for Rb/I/ or Cs/I/ ions. On ZAS, Rb/I/ shows a negative deviation above pH = 3 while a positive deviation is observed for Cs/I/ above pH = 5. SbS is highly selective for Rb/I/ above pH = 1 /$K_d = \infty$/. Thus, this material should be suitable for the separation of Rb/I/ from other alkali metals.

* *

The radioanalytical studies were performed in the Modular Laboratories of B.A.R.C., Bombay /India/ for which Dr. M. Sankar Das, Head of Analytical Chemistry Division and Dr. R.K. Iyer are thanked. Financial assistance provided by the C.S.I.R., India is gratefully acknowledged.

REFERENCES

1. C.B. Amphlett, Inorganic Ion Exchangers, Elsevier, Amsterdam, 1964.

2. V. Vesely, V. Pekarek, Talanta, 19 /1972/ 1245 and references therein.

3. A. Clearfield, G.H. Nancollas, R.H. Blessing, in Ion Exchange and Solvent Extraction, Vol. 5, J.A. Marinsky, Y. Marcus /Eds./, Marcel Dekker, New York, 1973, Ch. 1.

4. N.J. Singh, S.N. Tandon, J. Radioanal. Chem., 49 /1979/ 195.

5. J. Mathew, S.N. Tandon, J. Radioanal. Chem., 27 /1975/ 315.

6. K.G. Varshney, A.A. Khan, J.B. Jain, S.S. Varshney, Indian J. Technol., 19 /1981/ 457.

7. K.G. Varshney, A. Premadas, Sepn. Sci. and Technol., 16 /1981/ 793.

8. K.G. Varshney, S. Agrawal, K. Varshney, Sepn. Sci. and Technol., 18 /1983/ 39.

9. K.G. Varshney, U. Sharma, S. Rani, A. Premadas, Sepn. Sci. and Technol., 17 /1982/ 1527.

10. K.G. Varshney, S. Agrawal, K. Varshney, U. Sharma, S. Rani /unpublished work/.

Journal of Radioanalytical and Nuclear Chemistry, Articles, 82/2 (1984) 299–308

2.22 RADIATION STABILITY OF SOME THERMALLY STABLE INORGANIC ION EXCHANGERS

K. G VARSHNEY, S. AGRAWAL, K. VARSHNEY, U. SHARMA, S. RANI

Analytical Laboratory, Chemistry Section,
Faculty of Engineering and Technology,
Aligarh Muslim University,
Aligarh-202001 (India)

(Received June 22, 1983)

Effect of various doses of gamma radiation on the ion-exchange capacity, distribution coefficient values, elution behaviour, pH titration and infrared spectra of some thermally stable inorganic ion exchangers has been studied systematically. No change has been observed in the ion-exchange capacity, elution behaviour and the infrared spectra of the materials irradiated up to a total dose of $3 \cdot 10^8$ rad, while, a change has been observed in their pH-titration and distribution behaviour

Introduction

A large number of inorganic materials possessing ion-exchange properties have been synthesized and used for various separations of analytical and radiochemical importance [1-5] They are of growing interest in relation to the treatment of contaminated water or coolant moderator in reactors working at high temperatures and pressures,[1] as it is generally believed that they are resistant to heat and radiations However, very few reports[5-8] have appeared in the literature confirming this belief. ZSINKA et al [9] have shown that a generalization about the resistance of inorganic ion exchangers against radiations cannot be made, as supported by TANDON et al.[10]

We have synthesized some ion-exchange materials based on Si, P and As, which have shown promising ion-exchange behaviour[11-16] and high thermal and chemical stability. Their radiation stability has been studied by varying the total dose from 10^8 to $3 \cdot 10^8$ rad and observing the effect on their ion-exchange properties. This work is summarized in the following.

Experimental

Reagents and chemicals

All the reagents and chemicals used were of analar grade obtained either from the B D H Poole (England) or E. Merck (Darmstadt).

Instrumentation

pH measurements were made on an Elico (India) model LI-10 pH meter while I. R. studies were performed on a Beckman IR-20 spectrophotometer.

Ion-exchange materials and their synthesis

The various inorganic ion exchangers used in these studies are given in Table 1. They were prepared by standard methods already reported in the literature, which involve the precipitation of the material, filtration through a vacuum pump, drying at a particular temperature (45 °C), cracking in demineralized water (DMW) and then converting into the H^+ form by treatment with a dilute HNO_3 solution. The salient features of the preparation procedures, compositions and the ion-exchange capacities of these materials are summarized in Table 1.

Irradiation

The ion-exchange materials in H^+ form were irradiated with doses of $1 \cdot 10^8$, $2 \cdot 10^8$ and $3 \cdot 10^8$ rad at a dose rate of 0.4M rad/h using ^{60}Co as a source and $FeSO_4$ as a dosimeter.

Change of properties of the ion exchangers by γ-irradiation

Ion-exchange capacity. The Na^+ ion-exchange capacity (i.e.c.) was determined by the column process as follows:

One gram of the ion-exchange material in H^+ form was packed in a glass tube with an internal diameter of 0.6 cm, fitted with glass wool at its bottom. 250 ml of 1M $NaNO_3$ was then passed through this column at a low flow rate (0.4 ml/min) and the effluent was titrated with a 0.1M NaOH solution. The strong-acid capacities expressed in terms of milliequivalents per dry gram (meq/dry g) of the different samples before and after γ-irradiations, are shown in Fig. 1.

Elution behaviour. Earlier observations have shown that 250 ml of a 1M $NaNO_3$ solution is sufficient to completely elute H^+ ions from a column of the ion-exchange material (1 g), out of which the first 100 ml effluent contained the major amount (70–90%). This volume (100 ml) was, therefore, selected for eluting the H^+ ions

Table 1
Preparation, composition and ion-exchange capacity of the inorganic ion exchangers used

Ion-exchange material	Components, their concentrations, and *mixing ratios*			Chemical composition of the ion exchanger	Ion-exhange capacity, meq/dry g	Reference
Zirconium(IV) arsenosilicate (ZAS)	0.1M $ZrOCl_2$: 1	0.1M H_3AsO_4 : 1	1.0M Na_2SiO_3 : 1	Zr : As : Si 1 : 2 : 1	1.30	12
Zirconium(IV) arsenophosphate (α-ZAP)*	0.05M $ZrOCl_2$: 1	0.05M Na_2HAsO_4 : 1	0.05M Na_3PO_4 : 1	Zr : As : P 2 : 1 : 1	1.03	13
Tin(IV) arsenosilicate (SAS)	0.1M $SnCl_4$: 1	1.0M H_3AsO_4 : 1	0.1M Na_2SiO_3 : 1	Sn : As : Si 1 : 1 : 1	1.25	14
Thorium(IV) phosphosilicate (TPS)	0.1M $Th(NO_3)_4$: 1	1.0M H_3PO_4 : 1	0.1M Na_2SiO_3 : 1	Th : P : Si 1 : 1 : 1	1.66	15
Antimony(V) silicate (SbS)	0.1M $SbCl_5$: 2	0.1M Na_2SiO_3 : 1		Sb : Si 2 : 1	1.60	16

*Thermally treated phase of the normal sample prepared in this Laboratory earlier.[11]

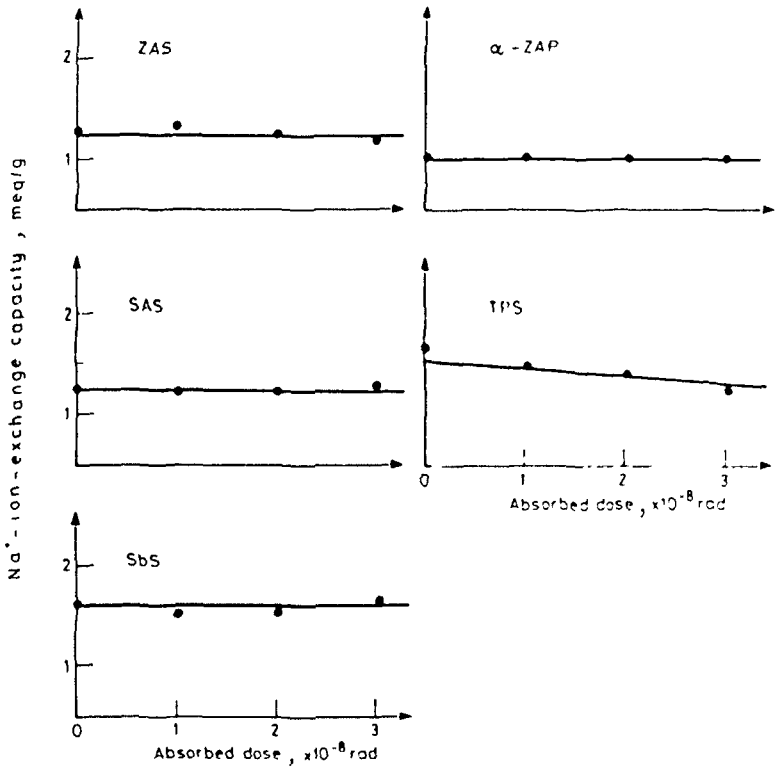


Fig. 1. Effect of γ-irradiation on the i.e.e. of some inorganic ion-exchangers

from various ion-exchange columns, maintaining the above flow rate for a comparative study of the elution behaviour. The effluent was titrated with a standard alkali solution for the presence of H^+ ions released and the percent release (R) was calculated as follows:

$$R = \frac{\text{Milliequivalents of } H^+ \text{ ions released in 100 ml}}{\text{Milliequivalents of } H^+ \text{ ions released in 250 ml}} \times 100$$

The value of R was then plotted against the total dose given to the material, as shown in Fig. 2.

pH titrations. 500 mg of the exchanger was taken in each of several 250 ml conical flasks followed by equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratios, the final volume being 50 ml to maintain the ionic strength constant (0.05M). The pH of the solution recorded after equilibrium

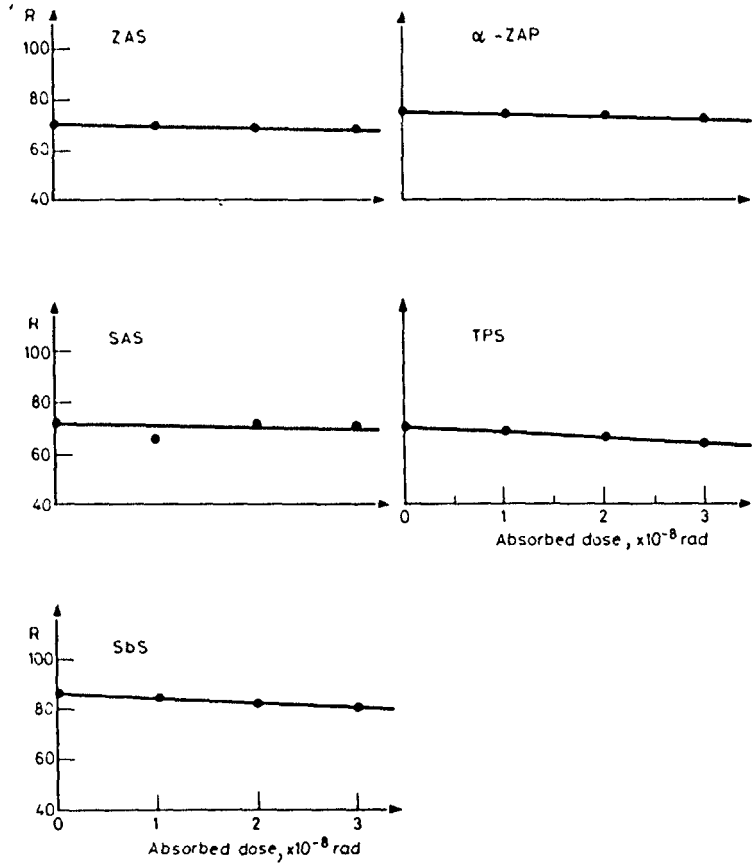


Fig. 2. Effect of γ-irradiation on the elution behaviour of some inorganic ion-exchangers

(attained in 24 hrs of standing at room temperature or by shaking for 3–4 hrs) was plotted against the milliequivalents of OH^- ions added. Fig. 3 shows pH titration curves for the normal and irradiated samples.

Distribution studies on the alkaline earth metals

Distribution studies were performed for the alkaline earth metals Mg(II), Ca(II), Sr(II) and Ba(II) in DMW and $HClO_4$ media as follows:

250 mg of the exchanger in H^+ form was equilibrated with 25 ml of the selected solvent, adjusting the initial metal ion concentration in the solution to a value not

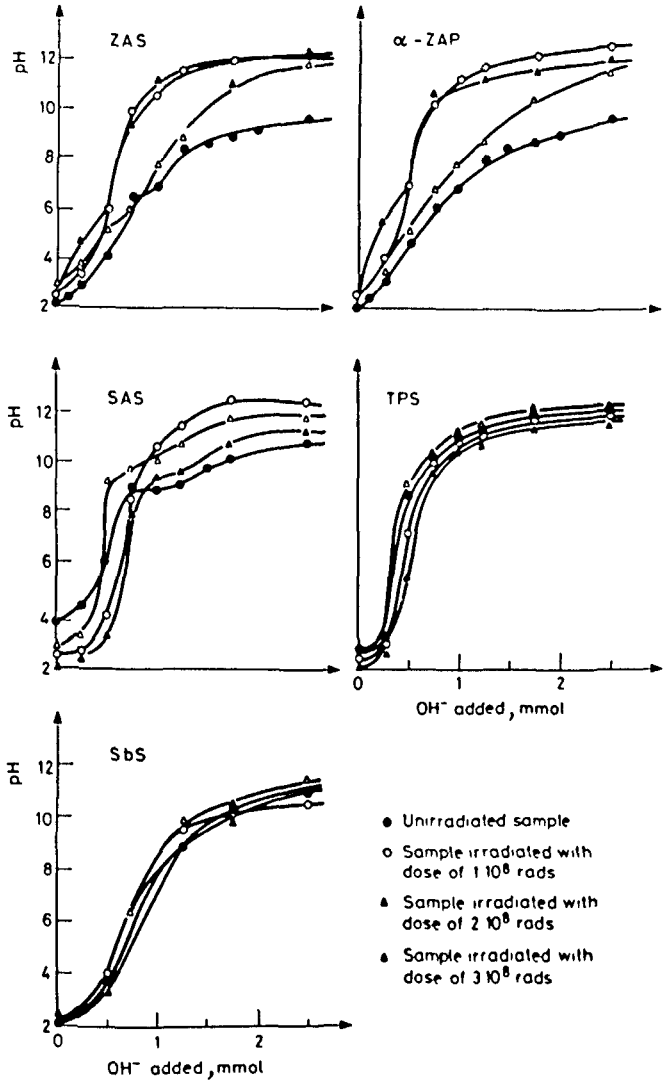


Fig. 3. Effect of γ-irradiation on the pH titration behaviour of some inorganic ion-exchangers

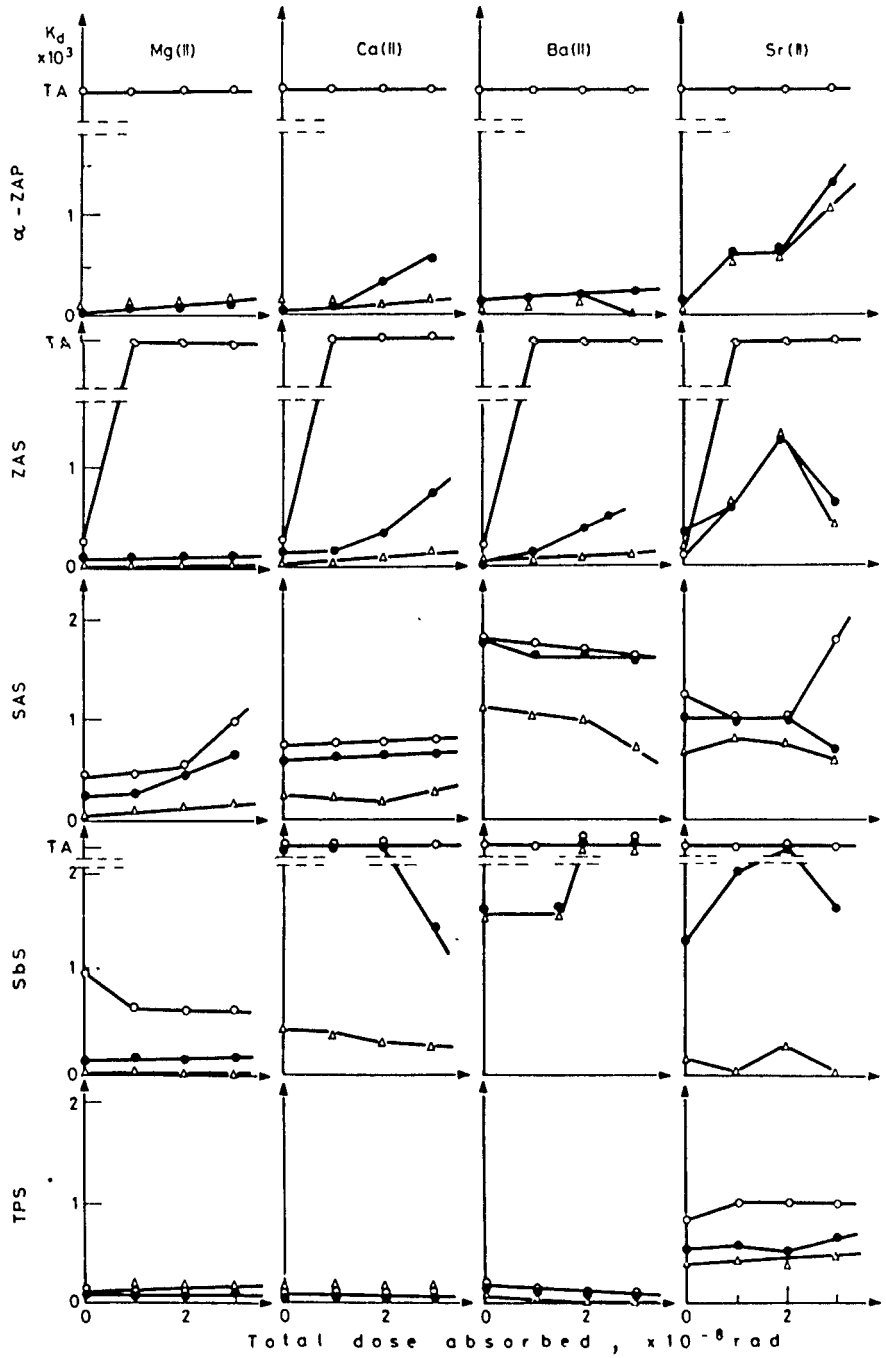


Fig. 4. K_d value as a function of the total dose absorbed by some inorganic ion-exchangers in DMW and $HClO_4$ media. Curves: o – DMW; • – 0.01M $HClO_4$; Δ – 0.10M $HClO_4$

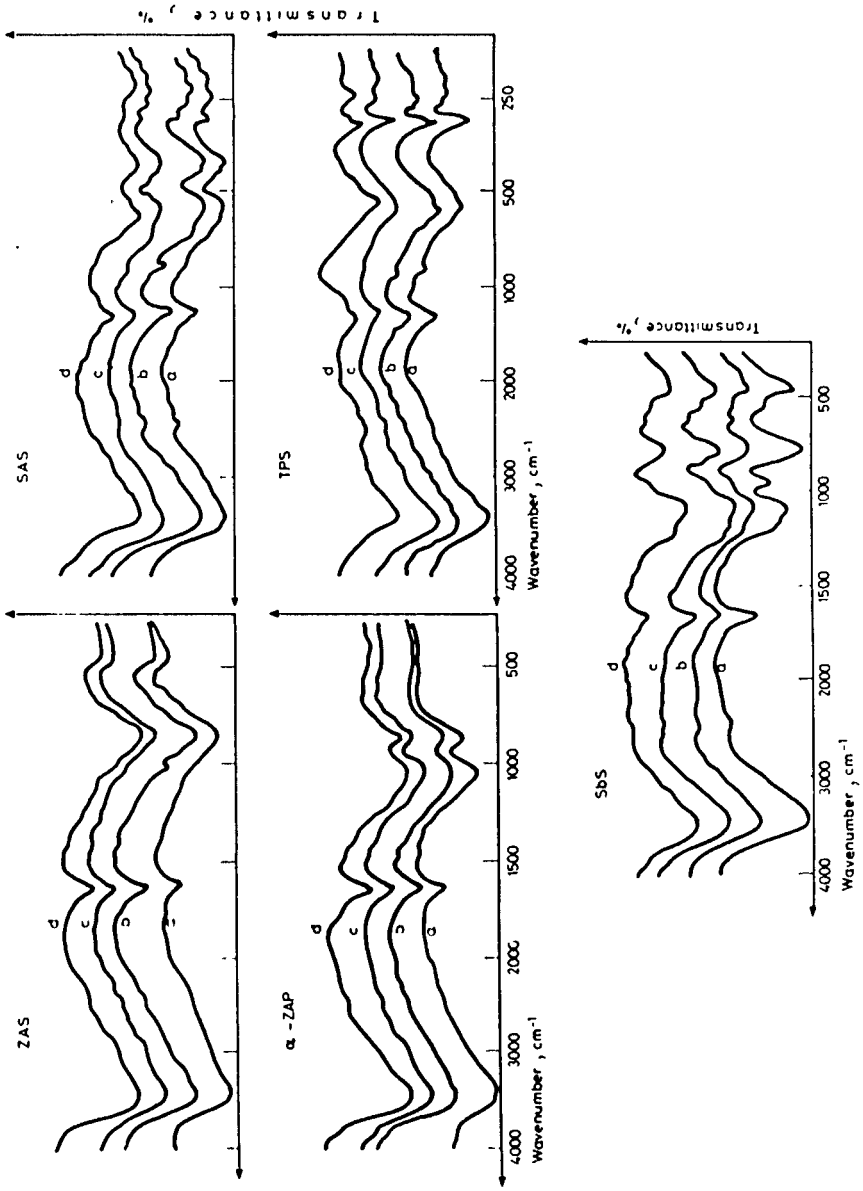


Fig. 5. I.R. spectra of various irradiated (b, c, d) and unirradiated (a) samples of some inorganic ion-exchangers. Total dose absorbed: b – $1 \cdot 10^8$ rad; c – $2 \cdot 10^8$ rad; d – $3 \cdot 10^8$ rad

exceeding 3% of the total i.e.c. of the material. The determinations were done with EDTA as usual. The K_d values were obtained from the expression,

$$K_d = \frac{(1 - F)}{F} \cdot \frac{V}{m} \text{ ml} \cdot \text{g}^{-1}$$

where F is the fraction of the metal ions present in the solution after equilibrium, V is the volume (ml) of the solution and A is the amount (g) of the exchanger. Fig. 4 shows the effect of γ-irradiation on the K_d values of the alkaline earths on various ion exchangers in different media.

Infrared studies

Fig. 5 gives the infrared spectra of various irradiated samples along with the normal ones.

Discussion

These studies reveal that the materials selected are highly resistant to radiations as far as their ion-exchange capacity and elution behaviour are concerned, except TPS, which shows a slight variation in these properties with an increase in the absorbed dose (Figs 1 and 2). In this respect they are different from their organic counterparts which undergo[7] ~15% loss in their i.e.c. on such a treatment. Also, no appreciable change has been observed in their infrared spectra (Fig. 5), indicating no significant structural changes.

pH titration curves, however, indicate a change (Fig. 3) on irradiation. The increase in pH is sharper for the irradiated samples containing arsenate group (ZAS, α-ZAP and SAS) than for the normal samples. TPS and SbS, however, do not show any significant change in this behaviour.

An interesting feature is observed in the distribution behaviour of these materials on irradiation. The K_d values obtained in different media (Fig. 4) for the four alkaline earths, generally, increase with the total dose absorbed. Also a complete reversal in K_d values is observed in ZAS. It shows a total adsorption of the alkaline earths in DMW after irradiation while on its normal sample these metals have low K_d values.

This reversal in the distribution behaviour is helpful in achieving some binary separations. For example, a normal sample of ZAS gives almost similar K_d values for the four alkaline earths in 0.01 and 0.1M $HClO_4$ while an irradiated ($2 \cdot 10^8$ rads) one gives a high selectivity for Ba(II). Hence, this ion can be separated from the rest of the alkaline earths on the irradiated ZAS columns. A similar behaviour is shown

by α-ZAP in these media. SbS, however, shows a peculiar distribution behaviour in 0.01 and 0.1M $HClO_4$ media. Irradiation lowers the K_d value of Ca(II) but that not of Mg(II). Similar observations are made for Sr(II) and Ba(II) on this exchanger. TPS and SAS, however, do not show any appreciable change in their distribution behaviour in all the three media studied after irradiation.

The authors are thankful to Prof. Mohsin QURESHI for the research facilities and to the C.S.I.R. (India) for financial assistance. The irradiation studies were performed in the Chemical Laboratories of Dr. B. S. M. RAO, Poona University, Pune, India.

References

1. C. B. AMPHLETT, Inorganic Ion Exchangers, Elsevier, Amsterdam, 1964.
2. S. J. NAQVI, D. HUYS, L. H. BAETSLE, J. Inorg. Nucl. Chem., 33 (1971) 4317.
3. V. VESELY, V. PEKAREK, Talanta, 19 (1972) 1245, and references therein.
4. A. CLEARFIELD, G. H. NANCOLLAS, R. H. BLESSING, in Ion Exchange and Solvent Extraction, Vol. 5, J. A. MARINSKY, Y. MARCUS (Eds), Marcel Dekker, New York, 1973, Ch. 1.
5. N. J. SINGH, S. N. TANDON, J. Radioanal. Chem., 49 (1979) 195.
6. C. B. AMPHLETT, Proc. 2nd Intern. Conf. Peaceful Uses of Atomic Energy, Geneva, 7 (1956) 490.
7. L. ZSINKA, L. SZIRTES, V. STENGER, Radiochem. Radioanal. Lett., 4 (1970) 257.
8. J. S. GILL, S. N. TANDON, Radiochem. Radioanal. Lett., 14 (1973) 379.
9. L. ZSINKA, L. SZIRTES, J. MINK, A. KALAMA, J. Inorg. Nucl. Chem., 36 (1974) 1147.
10. J. MATHEW, S. N. TANDON, J. S. GILL, Radiochem. Radioanal. Lett., 30 (1977) 381.
11. K. G. VARSHNEY, A. PREMADAS, Sepn. Sci. & Technol., 16 (1981) 793.
12. K. G. VARSHNEY, S. AGRAWAL, K. VARSHNEY, Sepn. Sci. & Technol., 18 (1983) 59.
13. K. G. VARSHNEY, K. VARSHNEY, S. AGRAWAL, Sepn. Sci. & Technol., (in press).
14. K. G. VARSHNEY, A. A. KHAN, A. MAHESHWARI, S. ANWAR, U. SHARMA, Ind. J. Technol., (in press).
15. K. G. VARSHNEY, U. SHARMA, S. RANI, (unpublished work).
16. K. G. VARSHNEY, U. SHARMA, S. RANI, A. PREMADAS, Sepn. Sci. & Technol., 17 (1982) 1527.

Reprinted from

Journal of Chromatography
Elsevier Publishing Company, Amsterdam - Printed in The Netherlands

CHROM. 5337

2.23

SYNTHESIS, ION-EXCHANGE BEHAVIOUR AND COMPOSITION OF TIN(IV) HEXACYANOFERRATE(II)*

MOHSIN QURESHI, K. G. VARSHNEY AND A. H. ISRAILI
Z.H. College of Engineering and Technology and Department of Chemistry, Aligarh Muslim University, Aligarh, U.P. (India)

(Received February 16th, 1971)

SUMMARY

Tin(IV) hexacyanoferrate(II) as an inorganic ion exchanger has been prepared in thirteen different ways by varying the pH, the mole ratios mixed and the concentration. Exhaustive analytical studies of a sample having a Sn/Fe mole ratio of 3:1 and an ion-exchange capacity of 2.02 mequiv./g dry weight have been made. These include investigation of its stability in different solvents and its composition, pH-titrations, ion distribution studies, thermogravimetry, and X-ray diffraction measurements. On the basis of all these experimental data a tentative approach to the formula of the compound was made. The potentiality of its use as an ion exchanger has been demonstrated by the achievement of some important and difficult separations.

INTRODUCTION

Metal ion complexes formed with ferrocyanides have recently shown very interesting properties as synthetic inorganic ion exchangers[1]. They are easily prepared and are comparatively less prone to the adverse effects of acids[2] and heat than organic ion exchangers. A high exchange capacity and the fact that they can be used for the separation of radioactive waste and fissionable materials[3] with less damage by radiation than their organic counterparts is indicative of their usefulness. The work on these ion exchangers reported so far mostly concerns their preparation, radiochemical properties, crystallography[4] and the adsorption behaviour of alkali metal ions or alkaline earths[5,6]. The ion-exchange adsorption of other ions has received less attention.

Tin(IV) ion exchangers prepared in these laboratories[7-11] have been found to show very good ion-exchange properties and a few very important and difficult separations have been achieved on papers impregnated with these materials[12,13]. So far, no systematic work on tin(IV) hexacyanoferrate(II) seems to have been reported in the literature. The formation of a yellow precipitate on the addition of

* A part of the paper was presented at the Convention of Chemists held at Kharagpur (India) in December, 1969.

potassium ferrocyanide solution to stannic chloride solution has been mentioned (see MELLOR[14]) but a detailed study of its use as an ion exchanger is lacking. The preparation and study of the properties of this material were undertaken and the results of such a study are summarized here.

EXPERIMENTAL

Reagents

Stannic chloride pentahydrate (Poland) and potassium ferrocyanide (B.D.H. Analar) were used. All other chemicals were of reagent grade.

Apparatus

Spectrophotometric studies were performed on a Bausch and Lomb spectronic 20 colorimeter. pH-measurements were made on Beckman model-G and Elico Model LI-10 pH-meters. A Philips Camera with an X-ray unit was used for the X-ray studies while thermogravimetry was performed with Stanton thermobalance type H-4.

Synthesis

Thirteen samples were prepared by mixing stannic chloride with potassium ferrocyanide solution under different conditions. The gels formed were digested at room temperature for 24 h. The supernatant liquid was then decanted and the gels were washed several times with distilled water to remove the unreacted reagents. They were filtered and dried at 40–45°. The dry gels were immersed in cold water. They broke down to small particles with cracking and slight evolution of heat. The exchanger was washed with hot distilled water at pH 6–7 to get rid of occluded tin ions or ferrocyanide. It was, then, immersed in 1–2 *M* HNO_3 or HCl for 24 h to convert it to the H^+ form. The exchanger in the H^+ form was washed with distilled water to remove excess acid. When the wash solution had a pH of 6–7 the samples were dried at 40–45°. The particles of desired size were then obtained by passing the ion-exchange material through appropriate sieves. The methods of preparation and some important properties of the different samples are summarized in Table I.

RESULTS

In order to prepare an ion exchanger having a high ion exchange capacity and low solubility, all the samples prepared were studied on a comparative basis. Their ion-exchange capacity, solubility in distilled water, and compositions are given in Table II.

As is clear from Table II, the ion exchange capacity increases with an increase of the ferrocyanide content in the product. However, the gel character improves with an increase in the tin content of the compound. S-11 was therefore selected for detailed study.

Properties

Tin(IV) hexacyanoferrate(II) (Sample S-11) is in the form of blue black, hard, shining granules, suitable for column operation.

TABLE I

SYNTHESIS OF DIFFERENT SAMPLES UNDER DIFFERENT CONDITIONS

Sample No.	*Method of preparation*	*Remarks*
S-1	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:1), pH 4	Green product
S-2	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (2:1), pH 4	Blue product
S-3	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:2), pH 4	Blue product which dissolved during washing
S-4	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:3), pH 4	Blue product which dissolved during washing
S-5	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:1), pH 1	Blue product
S-6	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:1), pH 6.9	Brown product having shiny particles
S-7	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:1), pH 9.9 (ammonia)	Brown product which dissolved in 1–2 *M* HCl in 24 h
S-8	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (1:1), pH 13 (NaOH)	Very small white precipitate which dissolved during digestion
S-9	0.02 *M* $SnCl_4$ + 0.02 *M* $K_4Fe(CN)_6$, (1:1), pH 1	Blue product
S-10	0.01 *M* $SnCl_4$ + 0.01 *M* $K_4Fe(CN)_6$, (1:1), pH 1	Blue product
S-11	0.1 *M* $SnCl_4$ + 0.1 *M* $K_4Fe(CN)_6$, (3:1), pH 0.8	Blue black, shiny particles
S-12	0.04 *M* $SnCl_4$ + 0.04 *M* $K_4Fe(CN)_6$, (3:2), pH 1.3	Blue black, shiny particles
S-13	0.02 *M* $SnCl_4$ + 0.02 *M* $K_4Fe(CN)_6$, (2:1), pH 1.6	Blue black, shiny particles

Chemical stability

To test the chemical stability visually, 0.2–0.5 g of the exchanger was kept in 25 ml of various solutions at room temperature with the following results:

(a) In 12 h there was no change with sulphuric acid, nitric acid, formic acid and acetic acid of all possible concentrations; 4 *M* hydrochloric acid, 0.02 *M* sodium hydroxide and 10% aqueous oxalic acid solutions.

TABLE II

A COMPARISON OF THE ION-EXCHANGE CAPACITY, SOLUBILITY AND COMPOSITION OF THE DIFFERENT SAMPLES

Sample No.	*Composition (Sn:Fe) (mole ratio)*	*Ion-exchange capacity mequiv./dry g*	*Solubility in water*	
			mg Sn/50 ml	*mg Fe/50 ml*
S-1	9.2:1	0.60	0.112	0.50
S-2	3.2:1	1.30	0.112	0.60
S-5	3:5	2.29	0.084	0.50
S-6	100:1	0.11	0.120	0.00
S-9	4:5	3.40	0.240	0.60
S-10	4:5	2.95	0.056	0.70
S-11	5:2	2.02	0.068	0.50
S-12	7:5	2.5	0.120	0.45
S-13	5:2	1.97	0.068	0.70

(b) In 15 min the exchanger dissolved in concentrated hydrochloric acid and 10% ammonium hydroxide.

A detailed study of the chemical stability of the exchanger in water and acids was made as follows:

It was first washed with hot water to remove any tin ions or ferrocyanide remaining adsorbed on the beads. 500 mg of this washed material were then refluxed with 50 ml of distilled water at different time intervals ranging from 1 to 8 h. On quantitative determination of tin and iron in all the filtrates it was noticed that there was a gradual increase in the amount of the dissolved ion exchanger in all cases and after heating for 8 h the exchanger had dissolved almost completely, giving a turbid blue solution. The solubility was determined in different solvents by taking 500 mg of the exchanger in 50 ml of the solvent, and refluxing it with an air condenser for 1 h in each case. After cooling, the solution was filtered and the tin and iron in the filtrate were determined spectrophotometrically by the procedures given below:

Determination of tin. 25 ml of the filtrate were distilled[15] to separate tin from iron. The distillate was diluted to 100 ml with distilled water in a standard flask. 0.5 ml (2:1) sulfuric acid and 5 ml conc. nitric acid were added to a 25 ml portion of the dilute distillate in a 100 ml beaker which was covered with a watch glass and heated to evaporate the liquid completely to dryness. The residue was then cooled and tin was determined with phenyl fluorone as usual[16] against a blank prepared in an identical manner.

Determination of iron. 10 ml of the filtrate were heated in a beaker with 1 ml of conc. H_2SO_4 and 1 ml of conc. HCl to decompose ferrocyanide and cyanide ions. The volume was reduced to about 1 ml and the solution was finally evaporated to dryness. The residue was taken up in a little distilled water and was transferred to a 10 ml standard flask. Iron was determined with 1,10-phenanthroline against a blank[17].

The results of the solubility determinations in water and acids are given in Table III.

Composition

200 mg of the exchanger were heated with 10 ml of H_2SO_4 and 50 ml of HCl. First the solution was blue (ferrocyanic acid) then it turned yellow. It was cooled and stannous chloride solution (60 g $SnCl_2$ in 600 ml HCl and 400 ml H_2O) was added

TABLE III

SOLUBILITY OF TIN(IV) HEXACYANOFERRATE(II) IN WATER AND ACIDS

Solvent	*Amount of tin dissolved in 50 ml (mg)*	*Amount of iron dissolved in 50 ml (mg)*
Distilled water	0.07	0.50
0.1 *M* HCl	0.42	1.75
0.1 *M* HNO_3	0.11	0.35
0.5 *M* HNO_3	0.19	0.35
1 *M* HNO_3	0.32	0.58
0.1 *M* H_2SO_4	0.38	1.58

TABLE IV

COMPOSITION OF TIN(IV) HEXACYANOFERRATE(II)

Wt. of the exchanger (mg)	*Volume of 0.1 N $K_2Cr_2O_7$ used for iron (ml) (a)*	*Volume of 0.1 N $K_2Cr_2O_7$ used for iron and tin (ml) (b)*	*Volume of 0.1 N $K_2Cr_2O_7$ used for tin only (ml) (b−a)*	*Molar ratio (Sn:Fe)* $\left\lfloor \frac{b-a}{2} : a \right\rfloor$
200	2.25	15.00	12.75	2.7:1
200	2.30	15.95	13.65	2.9:1
200	2.35	14.35	12.00	2.5:1
200	2.35	15.35	13.50	2.9:1
200	2.35	15.40	13.55	2.9:1

dropwise to the cold solution until the colour of iron was no longer evident. The excess of $SnCl_2$ was destroyed with mercuric chloride (saturated solution) as usual. 15 ml of a phosphoric acid–sulphuric acid mixture (150 ml H_3PO_4 + 150 ml H_2SO_4 diluted to 1000 ml) were then added and the volume was made up to about 200 ml with distilled water. Iron was determined by titration against a $K_2Cr_2O_7$ solution using diphenylamine as indicator[18].

For the simultaneous determination of tin and iron in the exchanger 200 mg were dissolved in the sulphuric acid–hydrochloric acid mixture as above. 10 ml of conc. H_2SO_4, 100 ml of conc. HCl and about 2–3 g of test lead in a 500 ml conical flask were added to this solution. The volume was made up to 300 ml with distilled water and the solution was heated for 1 h in an atmosphere of CO_2. It was then cooled to 10° in an ice bath. Tin and iron in the reduced state were titrated against 0.1 *N* $K_2Cr_2O_7$ using diphenylamine as the indicator[19]. The total quantity of tin and iron in the exchanger was thus determined. The amount of tin was then obtained by subtracting the quantity of iron from the total amount of tin and iron. The results for sample S-11 are summarized in Table IV.

Ion-exchange capacity

The gel was found to have cation-exchange properties. Its ion-exchange capacity was therefore determined by testing different mono- and bivalent metal ions in the usual manner[7,8]. A column was prepared in a glass tube of I.D. 6 mm and the flow rate of the effluent was kept at 10–12 drops (approx. 0.5–0.6 ml) per min. Table V summarizes the results.

TABLE V

ION EXCHANGE CAPACITY OF TIN(IV) HEXACYANOFERRATE(II)

Metal ion	*Capacity (mequiv./g dry exchanger)*
Na(I)	2.02
K(I)	2.08
Ba(II)	2.028
Mg(II)	1.88

Titration curve

Several 250 ml conical flasks, each containing 0.5 g of the exchanger, were taken. 0.1 *M* sodium hydroxide and 0.1 *M* sodium chloride were added in different ratios keeping the final volume at 100 ml in all cases. The flasks were kept for 3 days at 25°± 1° with intermittent shaking. After attainment of equilibrium the pH values of all the solutions were measured. The results are shown in Fig. 1.

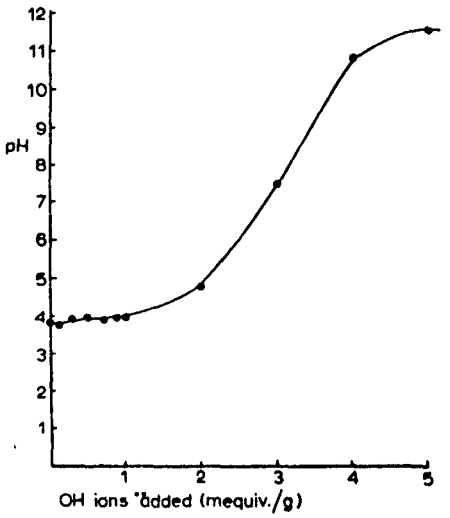


Fig. 1. Titration curve for stannic ferrocyanide.

Distribution coefficients

The usefulness of this exchanger for analytical separations was examined by determining the distribution coefficient with different metal ions in distilled water and 0.1 *M* nitric acid. The following method was used:

2 ml of the metal solution and 98 ml of either water or 0.1 *M* nitric acid were taken in a 250 ml conical flask. The concentration of the solution was adjusted so that the amount of the metal did not exceed 3% of the total capacity of the exchanger[20]. Then 0.5 g of the exchanger in H^+ form was added. The flask was kept at room temperature (25°± 1°) for 48 h with occasional shaking. 40 ml of this solution were titrated against 0.002 *M* EDTA solution and K_d values of the metal ion were determined using the formula:

$$K_d = [M_R]/[M_{Sol.}]$$

where $[M_R]$ = amount of the metal ion adsorbed per gram of the exchanger,

$[M_{Sol.}]$ = amount of the metal ion left per unit volume of the solution.

Sodium and potassium were determined in the solution using radioactive tracers. Table VI summarizes all the K_d values.

Thermogravimetry

The results of thermogravimetric analysis of sample S-11 are given in Fig. 2. To check the effect of heat on the colour of the exchanger and on its ion-exchange

TABLE VI

DISTRIBUTION COEFFICIENTS OF SOME METAL IONS

Metal ion	*Compound used*	*K_d value*	
		In water	*In 0.1 M HNO_3*
As(III)	Arsenite	0.0	0.0
Pb(II)	Nitrate	Total adsorption	1693
Cd(II)	Chloride	Total adsorption	1600
Cu(II)	Sulfate	2520	2520
Al(III)	Chloride	Total adsorption	230.4
Ga(III)	Chloride	1680	176
Ni(II)	Sulfate	Total adsorption	840
Co(II)	Chloride	Total adsorption	588.5
Mn(II)	Sulfate	Total adsorption	622.2
Zn(II)	Chloride	Total adsorption	1360.0
Ba(II)	Chloride	704.5	19.4
Sr(II)	Nitrate	1465.2	9.5
Ca(II)	Nitrate	484	0.0
Mg(II)	Nitrate	2470	5.3
K(I)	Chloride	52.6	17.4
Na(I)	Chloride	20.6	—
In(III)	Sulfate	21.4	0.0
Y(III)	Nitrate	8800	362.5
Fe(III)	Alum	156.9	10.9
Bi(III)	Nitrate	Total adsorption	120.0
Sm(III)	Chloride	1905.2	66.6
Nd(III)	Chloride	813.3	8.5
Pr(III)	Chloride	486.3	10.9

capacity 1 g portions of S-11 were heated at 100, 200, 300 and 400° for 1 h in each case. Capacities of all the samples after heating were determined in the usual way. The results are shown in Table VII.

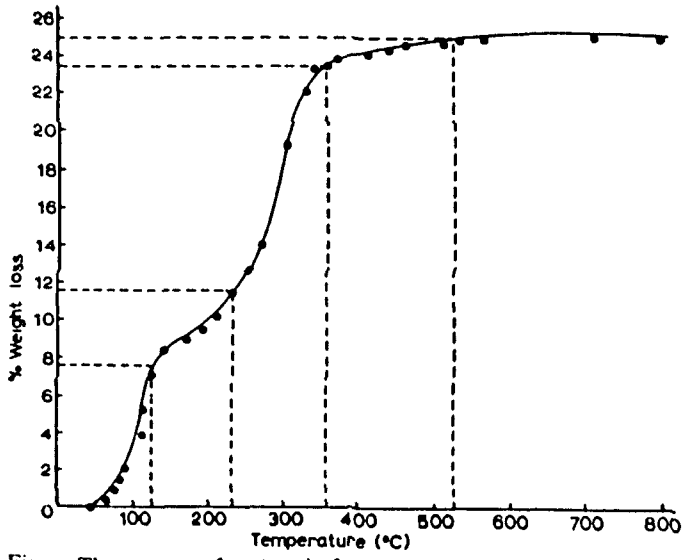


Fig. 2. Thermogram for stannic ferrocyanide.

TABLE VII

EFFECT OF HEAT ON THE EXCHANGER

Temperature (°C)	*Colour of the beads*	*Capacity (mequiv./g)*
Room temp.	Blue black	2.02
100	Blue black	2.02
200	Dirty black	0.60
300	Brownish black	0.02
400	Brown	0.01

X-ray diffraction studies

X-ray diffraction studies showed that tin(IV) hexacyanoferrate(II) is slightly crystalline at room temperature. The crystalline character increases as the temperature is raised, and at 400° a good X-ray pattern is observed.

DISCUSSION

From Tables I and II it is clear that in highly acidic solutions (pH 1) the molar ratio of tin and iron in the gel depends upon the volume ratio of mixing. At higher pH values (pH 4–7) the amount of tin present is always greater than the iron content of the sample. It is probably due to the formation of some tin hydroxide at the higher pH values. This inference is supported by the fact that the precipitates formed at pH 6.9 show Sn:Fe ratio as 100:1. Moreover the samples prepared at pH 10 and at pH 13 dissolve easily in acid solutions. On drying, all the gels turn blue black or prussian blue. This is perhaps due to a redox phenomenon taking place in the system which is indicated by the positive tests obtained for ferro- and ferricyanides in an alkaline solution of the exchanger. When the exchanger is, however, dissolved in a sulphuric acid hydrochloric acid mixture the solution does not give a positive test for these radicals. This may be due to the decomposition of ferrocyanide and the subsequent oxidation of Fe(II) to Fe(III) by oxygen dissolved in the solution. Such a solution, therefore, gives the test for iron in the trivalent state only. Furthermore, in acidic solutions potassium ferrocyanide forms ferrocyanic acid [$H_4Fe(CN)_6$]. Some of the iron in the bivalent state is oxidized to Fe(III), which with ferrocyanic acid, forms prussian blue $Fe_4[Fe(CN)_6]_3$ in the system, thus resulting in the blue coloured material.

On the basis of chemical and thermogravimetric analysis of the sample and the formula given for titanium(IV) ferrocyanide[21], the following formula for tin(IV) hexacyanoferrate(II) is proposed:

$$[(SnO)_3 \cdot (OH)_3 \cdot HFe(CN)_6 \cdot 3H_2O]_n$$

As shown by the above formula there is only one replaceable hydrogen atom per molecule which is attached to the $Fe(CN)_6^{4-}$ group. This is suggested by one inflection point observed in the titration curve of the exchanger (Fig. 1). The pyrolysis curve for stannic ferrocyanide (Fig. 2) confirms other aspects of the proposed formula. Thus, if this formula is considered to be correct and the percentage weight losses

which are indicated at each break of the curve, are correlated with certain chemical transformations taking place on heating, the following inferences are possible

(a) Three water molecules per mole of the exchanger are present as water of crystallization They are lost on heating it up to 125° giving a weight loss of 7 6% (theoretical weight loss of 7 5% due to the removal of 3 H_2O)

(b) Above 125° condensation of the molecule takes place which is indicated by a further loss of 4% in weight of the exchanger at 230° This loss corresponds to two water molecules which are removed from the structure (theoretical total weight loss of 12 4% at 230° due to the loss of 5 H_2O)

(c) Cyanogen begins to be evolved[22] at 237°, the steeper portion between 230° and 355° therefore corresponds to the decomposition of ferrocyanide and the loss of cyanide as cyanogen At 355° the total weight loss is 23 4% which closely resembles the theoretical weight loss (23 3%) if three cyanide radicals are assumed to be lost at this temperature

The portion between 355° and 525° corresponds to one cyanide radical only. It seems therefore that there are only four cyanide radicals available in one molecule of stannic ferrocyanide Two cyanide radicals must therefore be lost at lower temperatures This is supported by the fact that a smell of HCN is observed on drying the product

The titration curve (Fig 1) shows that when only NaCl is used it releases hydrogen ions and hence a sharp decrease of pH occurs On the addition of NaOH the pH increases rapidly and above pH 7 the exchanger begins to dissolve. On gradually increasing the volume of NaOH the rate of dissolution and hydrolysis of the exchanger increases and there is a corresponding increase in the pH of the solution This is perhaps due to the fact that the partial exchange of H^+ with Na^+ slows down the rate of exchange and the release of H^+ ions No appreciable change in pH is recorded above pH 12 1

The observed K_d values of metal ions (Table VI) show that this exchanger has a great affinity for Pb, Cd, Cu, Al, Ga, Ni, Co, Mn, Zn, Ba, Sr, Ca, Mg, Y, Bi, Sm, Nd, and Pr in aqueous solutions Sodium, potassium and indium have low K_d values, and therefore it is possible to separate them from other metal ions The adsorption of metal ions was also studied in 0 1 M HNO_3 which showed that the K_d value decreased as the hydrogen ion concentration increased This fact can be predicted if the ion-exchange reaction is defined by the equation

$$M^{n+}_{aq} + nHR \rightleftharpoons MR + nH^+$$

and

$$K_d = \frac{[M_R]}{[M^{n+}_{aq.}]}$$

where

$[M^{n+}_{aq}]$ = concn of metal ion in the solution,

$[M_R]$ = concn of metal ion in the exchanger

If the hydrogen ion concentration is increased the reaction will tend to proceed in the reverse direction and therefore the adsorption of the metal ion on the exchanger

is decreased Thus rare earths (Sm, Nd, Pr) which show high adsorption in aqueous medium, have very low K_d values in 0.1 M HNO_3. Similarly, Ba, Sr, Ca, and Mg lose their affinity for the exchanger in acid solutions. On the basis of the distribution studies the following separations are possible:

Alkali metals and alkaline earths from Pb(II), Cd(II), Cu(II), Al(III), Ga(III), Ni(II), Co(II), Mn(II), Zn(II).

Arsenic(III), which is taken as arsenite, is not adsorbed on the exchanger beads, obviously due to the cation-exchange behaviour of the material, which completely elutes the arsenite ion. This fact has successfully been utilized for the quantitative separation of arsenic from the metal ions which commonly interfere with this ion such as Pb(II), Cd(II), Cu(II), Ni(II), Co(II), Mn(II) and Zn(II).

ACKNOWLEDGEMENT

The authors are grateful to Dr. S. M. F. RAHMAN for research facilities

The Council of Scientific and Industrial Research, New Delhi (India) is thanked for financial assistance to K.G.V. during the progress of this work.

REFERENCES

1 S KAWAMURA, H KURAKU AND K KUROTAKI, *Anal. Chim Acta*, 49 (1970) 317
2 D HUYS AND L H BAETSLE, *J Inorg Nucl Chem*, 26 (1964) 1329.
3 L H BAETSLE D HUYS AND D VAN DEYCK, *J Inorg Nucl Chem.*, 28 (1966) 2385.
4 L H BAETSLE D VAN DEYCK AND D HUYS, *J Inorg Nucl Chem*, 27 (1965) 683
5 V KOURIM, J RAIS AND J STEJSKAL, *J Inorg Nucl. Chem*, 26 (1964) 1761
6 J KRTIL *J. Inorg Nucl Chem*, 27 (1965) 233, 1862
7 M QURESHI AND J P RAWAT, *J Inorg Nucl Chem*, 30 (1968) 305.
8 M QURESHI AND K G VARSHNEY, *J. Inorg Nucl Chem*, 30 (1968) 3081.
9 M QURLSHI R KUMAR AND H S RATHORE *J Chem Soc (A)*, (1970) 272
10 M QURESHI, H S RATHORE AND R. KUMAR *J Chem Soc (A)*, (1970) 1986
11 M QURESHI, H S RATHORE AND R KUMAR, *J. Chromatogr*, 54 (1971) 269
12 M QURESHI AND S Z QURESHI, *J Chromatogr*, 22 (1966) 198.
13 M QURESHI, I AKHTAR AND K. N MATHUR, *Anal Chem.*, 39 (1967) 1766.
14 J W MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol VII, Longman s Green, London, 1931, p. 338.
15 E B SANDELL, *Colorimetric Determination of Traces of Metals*, III revised ed , Interscience, New York, 1959, p 856
16 E. B SANDELL, *Colorimetric Determination of Traces of Metals*, III revised ed , Interscience, New York 1959, p 862
17 E B SANDELL, *Colorimetric Determination of Traces of Metals*, III revised ed , Interscience, New York 1959 p 541
18 W W SCOTT, *Standard Methods of Chemical Analysis*, Vol I, 5th ed , Van Nostrand, New York, 1939, p 473
19 I M KOLTHOFF AND R BELCHER, *Volumetric Analysis*, Vol III, Interscience, New York, 1957 pp 321–322
20 H HAMAGUCHI, R KURODA, K. AOKI, R SUGISITA AND N ONUMA, *Talanta*, 10 (1963) 151
21 K H. LEISER J BASTIAN, A B H HECKER AND W HILD, *J. Inorg Nucl Chem*, 29 (1967) 815
22 C DUVAL, *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, London, New York, 1953 p 73

2.24

Cation Chromatography on Tin (II) Hexacyanoferrate (II) Papers in HCl and HCl + NH_4Cl Systems. Prediction of Ksp Values from Ri Values

199

K. G. Varshney / S. S. Varshney

Chemistry Section, Z.H. College of Engineering and Technology, Aligarh Muslim University, Aligarh, India

Summary

Tin (II) hexacyanoferrate (II) papers have been used to study the chromatographic flow of metal ions in solvent systems containing different concentrations of HCl and NH_4Cl. The effect of parameters such as atomic number (Z), ionic charge, bare ionic radius (r^0) and solubility products of metal hexacyanoferrates (II) on the rate of movement of the ions has been studied. As a result, a linear relationship between Ri ((Rf on plain paper)·(Rf on impregnated paper)) and the solubility product (Ksp) of metal ferrocyanides has been obtained as follows:

$$Ri = 0.76 + 0.0027 \frac{10^3}{-\log Ksp \cdot Z^2 \cdot r^0}$$

The Ksp values of various hexacyanoferrates (II) have been predicted on the basis of the above relation.

Introduction

The use of hexacyanoferrate (II) compounds in the ion-exchange of metals has been long known [1–11] as they show very good scavenging properties. Tin (II) hexacyanoferrate (II) has been prepared in these laboratories [12] and its ion-exchange properties studied in detail. It was found to possess high exchange capacity and high chemical stability in comparison to other hexacyanoferrates, especially stannic hexacyanoferrate (II) [13]. Later the material was used for impregnating paper in order to obtain binary separations of metal ions [14], twenty three such separations being achieved. Thus, the material has shown potential in important and difficult separations. Apart from separations paper chromatography has also been useful as a means of obtaining physical data such as the determination of the solubility product Ksp using Rf values. *Qureshi* and *Sharma* [15] have used stannic arsenate papers in butanol-nitric acid media to predict Ksp values of metal arsenates. In these studies we have explored the possibility of predicting Ksp values of hexacyanoferrate (II) compounds from Ri values using tin (II) hexacyanoferrate (II) paper.

Experimental

Preparation of ion-exchange paper: Whatman No. 1 paper strips, 15 × 3.5 cm were impregnated with 0.25 mol dm^{-3} stannous chloride solution in 4 mol dm^{-3} HCl, dried and dipped in 0.25 mol dm^{-3} potassium hexacyanoferrate (II) at room temperature. Excess solution was drained off and the strips placed over a filter sheet. They were washed thoroughly to remove excess stannous chloride, potassium hexacyanoferrate (II), or the acid, and were used dry.

Test solutions and detection tests: the test solutions of metals and the solutions of detection reagents were prepared as described earlier [15].

Procedure. one or two drops of test solutions were applied with glass capillaries and the ascending technique used. The paper was conditioned for 15 minutes and development was with the solvent systems described under Results. The solvent ascent was always 11 cm.

Results

Rf values on plain papers as well as on the tin (II)-hexacyanoferrate (II) papers were noted in the following solvent systems:

1. HCl: 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 0.5 and 1.0 mol dm^{-3}
2. 1 mol dm^{-3} HCl + 1 mol dm^{-3} NH_4Cl in proportions: 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9.1.

The following 34 metals were used for chromatographic studies:
Cu (II), Ag (I), Rb (I), Mg (II), Ca (II), Sr (II), Ba (II), Zn (II), Cd (II), Hg (II), Al (III), In (III), Tl (I), Pb (II), La (III), Zr (IV), As (III), Se (IV), V (V), Cr (III), Mo (VI), W (VI), Mn (II), Co (II), Ru (III), Ni (II), Ir (III), Pt (IV), Ce (III), Ce (IV), Nd (III), Th (IV), U (VI).

Discussion

The main features of these studies are:

a) A relation between the Rf and Ri values of metal ions and their average charge and their atomic number.
b) A relation between the Ri values and the Ksp of various metal ferrocyanides.

In general it was found that the metal ions do not move much ($Rf \approx 0$) in most of the solvent systems, thus indicating a large value for the selectivity coefficient on the impregnated papers. This is consistent with our previous

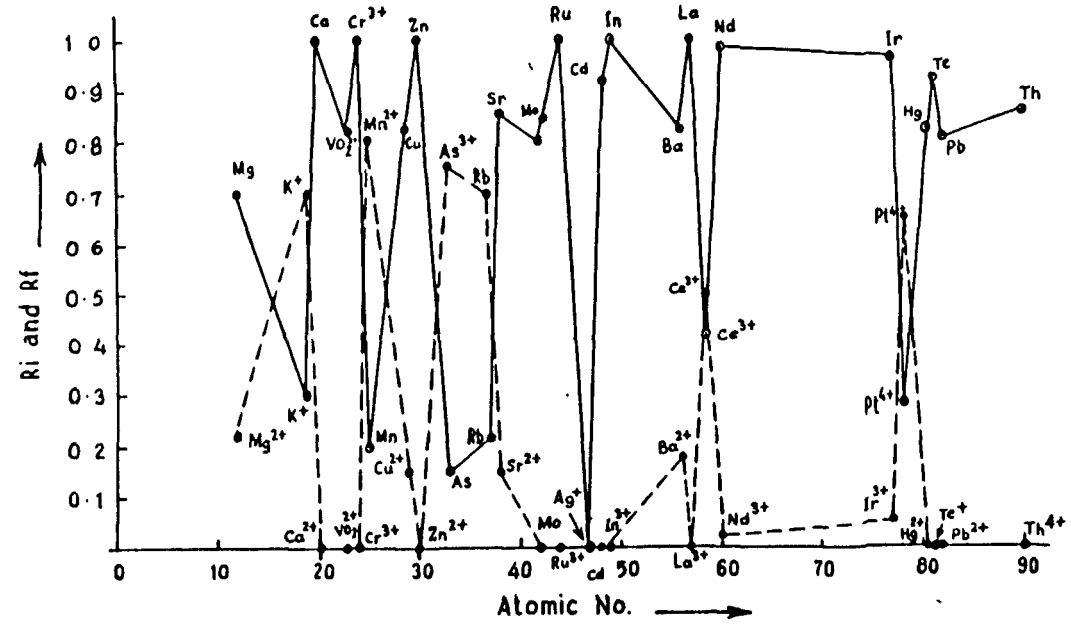


Fig. 1

● Ri and Rf versus atomic number in 10^{-1} mol dm^{-3} HCl. ●– – –● Rf values, o——o Ri values

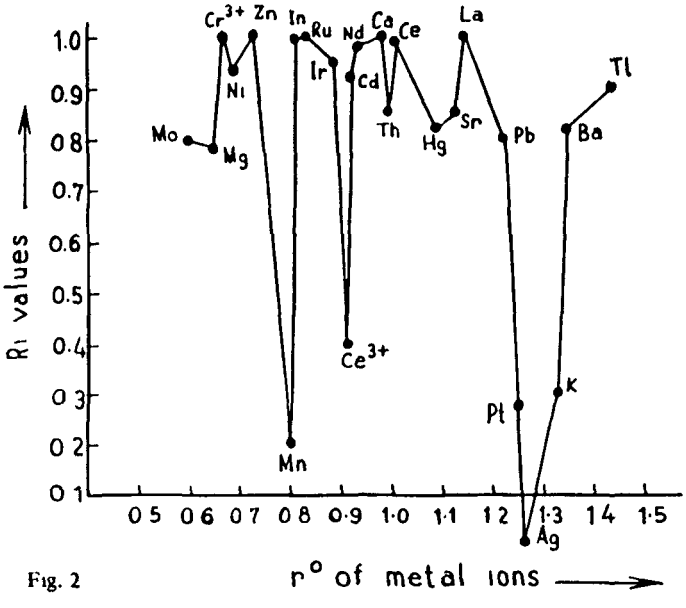


Fig. 2

Ri versus r^0 in 10^{-1} mol dm^{-3} HCl

conclusion that tin (II) hexacyanoferrate (II) is highly selective for metals owing to the formation of stable ferrocyanides.

In 0·1 mol dm^{-3} HCl the movement of ions is appreciable probably because of the lowered pH. A comparison of Rf with Ri (Fig. 1) reveals that K, Mn, As, Rb, Ag, Pt and Ce are the only metal ions for which Ri is small in comparison to other metals. Ag(I) is probably reduced by the cellulose of the paper to the metallic form. Arsenic and platinum are used as anions and, therefore, the exchange effect is not significant in these cases because tin(II) hexacyanoferrate (II) is a cation-exchanger. Mangenese and cerium hexacyanoferrate (II) may not be very stable under the conditions of the experiment and hence they decompose during the chromatographic process, making free ions available for exchange on the papers. Potassium and rubidium hexacyanoferrate (II) are soluble and hence show appreciable Rf values on impregnated papers. Addition of NH_4Cl to HCl systems has not been found to affect the movements significantly.

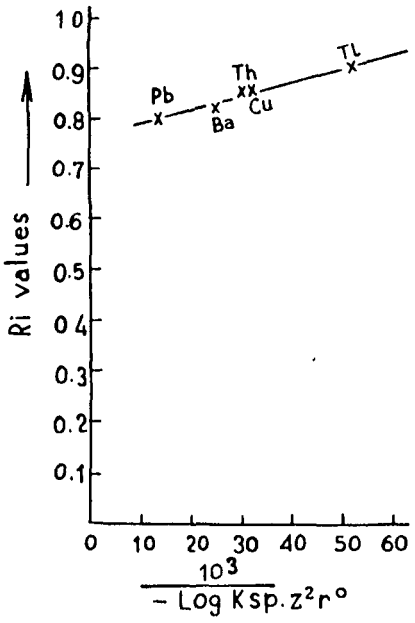


Fig. 3

● Ri versus $\frac{10^3}{-\log Ksp\, Z^2 r^0}$ in 10^{-1} mol dm^{-3} HCl

R_I is defined [16] as the difference between the Rf values on the plain and the impregnated papers It gives a real measure of ion exchange effects due to the presence of the ion exchange material on the paper It excludes the possible interactions of ions with the cellulose of the paper which is not the case with Rf value Therefore on papers loaded with the ion exchange material, R_I should be a more significant quantity than Rf The hydrated radius of the metal ion is also an important factor in ion-exchange chromatography It is inversely proportional to the bare ionic radius, a more fundamental characteristic of an element Hence the ion exchange phenomenon may establish a relationship between R_I and the bare ionic radius of a metal on impregnated papers A plot of R_I versus bare ionic radii (Fig 2) indicates this behaviour Also, solubility of metal hexacyanoferrates(II) is another factor that seems to effect the value of R_I or Rf on these papers In a similar study made earlier on stannic arsenate papers it was observed that these quantities, namely the charge on the metal ion, bare ionic radius, and the solubility product of the metal arsenates correlate with the Rf values Here, we observe that R_I also bears a relationship to these quantities on tin (II) hexacyanoferrate (II) papers A plot of R_I versus $10^3/-\log Ksp\, Z^2 r^0$ is a straight line (Fig 3) which gives the following relationship

$$R_I = 0\,76 + 0\,0027 \frac{10^3}{-\log Ksp\, Z^2 r^0}$$

Table I Experimental values of Ksp for some metal hexacyanoferrates (II)

Metal hexacyanoferrate (II)	Ksp
Th^{4+}	$6\,7 \times 10^{-9}$
Pb^{2+}	$3\,3 \times 10^{-16}$
Cu^{2+}	10^{-17}
Ba^{2+}	$3\,4 \times 10^{-8}$
Tl^{+}	$9\,2 \times 10^{-12}$

Table II Predicted values of Ksp of different metal hexacyanoferrates (II)

Metal hexacyanoferrate (II)	Ksp
Cd^{2+}	$4\,46 \times 10^{-5}$
Sr^{2+}	$3\,0 \times 10^{-7}$
Ca^{2+}	$1\,3 \times 10^{-3}$
La^{3+}	$8\,3 \times 10^{-2}$
Mg^{2+}	$1\,1 \times 10^{-52}$
Mo^{6+}	$7\,7 \times 10^{-4}$
Hg^{2+}	$6\,2 \times 10^{-11}$

Work is in hand to confirm the values in Table II experimentally

where Z is the charge on the metal ion, r^0, the bare ionic radius and Ksp the solubility product of the metal ferrocyanide Only those metals have been taken, whose hexacyanoferrate Ksp values are available in the literature [17, 18] namely Pb, Ba, Th, Cu and Tl (Table I). This formula can now be used to predict the Ksp values of various other hexacyanoferrates (II) (Table II)

Acknowledgement

The authors are thankful to Dr *R N Gupta* Principal, Hindu College, Moradabad, for facilities and encouragement The U G C, India, is gratefully acknowledged for the financial assistance to one of us (S S V)

References

[1] *G B Barton, J L Hepworth, E D Maclanahan,* Jr, *R L Moore* and *H H Tuyl,* Ind Eng Chem 50, 212 (1958)

[2] *N Mishio, A Khamoshida, S Kadoya* and *T Ishihara,* J At Energy Soc Jap 6, 2 (1964)

[3] *V Kourim* and *B Million,* Collect Czech Chem Commun 30, 2848 (1965)

[4] *L H Baetsle, D V Deyck* and *D Huys,* J Inorg Nucl Chem 27, 683 (1965)

[5] *J Krtil,* J Inorg Nucl Chem 27, 233 (1965)

[6] *J Krtil,* J Inorg Nucl Chem 27, 1862 (1965)

[7] *V Kourim, J Rais* and *B Million,* J Inorg Nucl Chem 26, 1111 (1964)

[8] *K Watari* and *M Izawa,* J Nucl Sci Technol (Tokyo) 2, 327 (1965)

[9] *K Watari, K Imai* and *M Izawa,* J Nucl Sci Technol (Tokyo) 4, 190 (1967)

[10] *S Kawamura, K Kurotaki, H Kuraku* and *M Izawa,* J Chromatog 26, 557 (1967)

[11] *V Kourim, J Rais,* and *J Steiskal,* J Inorg Nucl Chem 26, 1761 (1964)

[12] *M Qureshi, K G Varshney* and *Fehmida Khan,* J Chromatog 65, 547 (1972)

[13] *M Qureshi K G Varshney* and *A H Israili,* J Chromatog 59, 141 (1971)

[14] *M Qureshi, K G Varshney* and *Fehmida Khan,* Sep Sci 8, 279 (1973)

[15] *M Qureshi* and *S D Sharma,* Anal Chem 45, 1283 (1973)

[16] *M Qureshi, J P Rawat* and *Veena Sharma,* Talanta 20, 267 (1973)

[17] *A Belloma,* Talanta 17, 1109 (1970)

[18] *H Stephens* and *T Stephens* (Eds), Solubilities of Inorganic and Organic Compounds, Vol 1, part 1, pp 11, 34, 43, Pergamon Press New York 1963

Received Dec 6, 1976
Revised version received March 6, 1977
Accepted March 14, 1977

PROC. NAT. ACAD. SCI. INDIA, 59 (A), II, 1989

2.25

Chromatography of amino acids on papers impregnated with tin (IV) and thorium (IV) phosphosilicates : Separation of basic amino acids from others

(Key words : paper chromatography/amino acids/tin (IV)/phosphosilicates/thorium (IV)/phosphosilicates)

Abstract

Papers impregnated with tin (IV) and thorium (IV) phosphosilicate cation exchangers have been utilized for a chromatographic study of 24 amino acids using demineralized water, alcohols, acids, acetone, benzene, ether and phenol as developers. The study has resulted in the separation of basic amino acids from others.

Inorganic ion exchangers have found use in the metal analysis of some pharmaceuticals[1-6]. However they have received negligible attention for the separation of amino acids[7] which have great biochemical importance. The present communication summarizes our efforts to utilize tin (IV) and thorium (IV) phosphosilicates[8,9] in paper chromatographic study of amino acids. On this basis the separation of basic amino acids from others has been possible.

The following amino acids were used. They are reported in the increasing order of their molecular weight.

Neutral : Glycine (N_1), Hydroxyproline (N_2), Alanine (N_3), Aminobutyric acid (N_4), Serene (N_5), Proline (N_6), Valine (N_7), Threonine (N_8), Cystiene (N_9), Leucine (N_{10}), Isoleucine (N_{11}), Nor-leucine (N_{12}), Methionine (N_{13}), Tyrosine (N_{14}), Ph-Alanine (N_{15}), Tryptophan (N_{16}), Dopa (N_{17}), Cystine (N_{18}).

Basic : Ornithine (B_1), Lysine (B_2), Hystidine (B_3), Arginine (B_4).

Acidic : Aspartic acid (A_1), Glutamic acid (A_2).

Chromatography was performed on 15 x 3 cm of Whatman no. 1 paper strips in glass jars of 21 x 5 cm using the ascending technique. A. R. grade chemicals and reagents were used.

The paper strips were first impregnated in an aqueous 0.1 mole dm^{-3} stannic chloride solution for 3-5 s and dried for 30 min. on a filter paper to remove the excess reagent. These strips were then treated with aqueous 0.1 mole dm^{-3} sodium silicate for 3-5 s and again dried for 30 min. Then they were treated with a H_3PO_4–HNO_3 mixture (1 mole dm^{-3} in terms of each acid) for 5 s and allowed to dry at room temperature before washing with distilled water several times to remove the excess acids (SPS). The strips were ready for use after drying. Thorium phosphosilicate (TPS) papers were prepared in a similar manner by taking aqueous 0.1 mole dm^{-3} thorium nitrate instead of stannic chloride.

0.1% solution of cystine and 1% solution of other amino acids were prepared in demineralized water. A 2% alcoholic solution of ninhydrin was used as a detector. The solvents used were : Demineralized water (DMW), methanol, ethanol, n-butanol, formic acid,

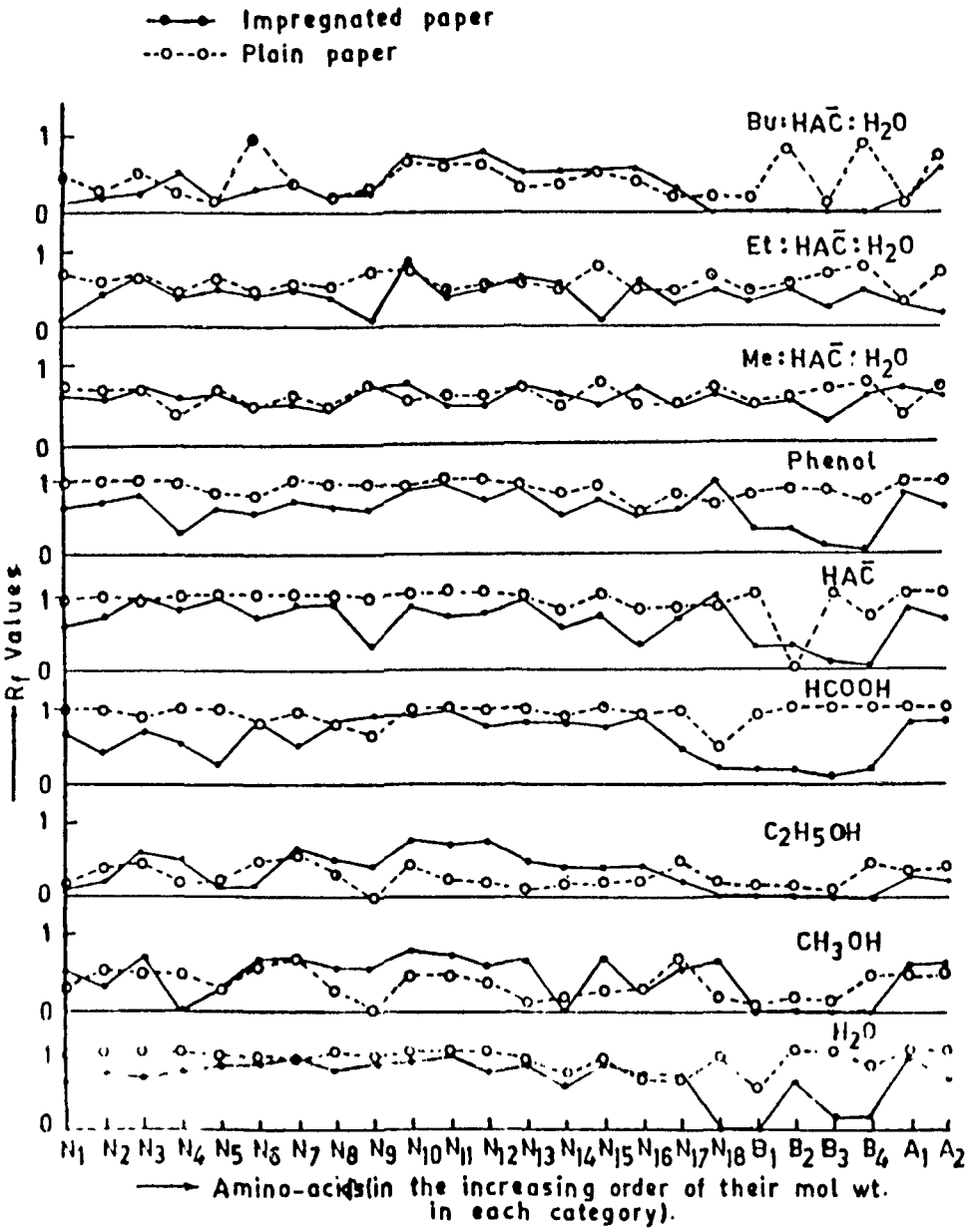


Fig 1 *Rf* spectra for amino acids in various solvent systems on plain and impregnated papers.

acetic acid, benzene, acetone, ether, phenol, methanol : acetic acid : DMW (4:1:5), ethanol . acetic acid : DMW (4:1:5) and butanol : acetic acid : DMW (4:1:5).

Table 1 – Some binary separations of amino acids on SPS papers.

Solvent system			Binary separations achieved
Methanol	Ornithine	–	Aspartic acid (0–0.57)
	"		Glutamic acid (0–0.56)
	"		Cysteine (0–0 58)
	"		Methionine (0–0 68)
	"		Phenylalanine (0–0.68)
	"		Glycine (0–0 51)
	"		Valine (0–0 75)
	"		Alanine (0–0.71)
	"		Proline (0–0 51)
	"		Leucine (0–0.70)
	Lysine	–	Aspartic acid (0–0.56)
	"		Glutamic acid (0–0.60)
	"		Cysteine (0–0 64)
	"		Methionine (0–0 72)
	"		Phenylalanine (0–0 62)
	"		Glycine (0–0 68)
	"		Valine (0–0 85)
	"		Alanine (0–0 68)
	"		Proline (0–0 63)
	"		Leucine (0–0 62)
	Histidine	–	Aspartic acid (0–0 55)
	"		Glutamic acid (0–0.60)
	"		Cysteine (0–0 47)
	"		Methionine (0–0 67)
	"		Phenylalanine (0–0 63)
	"		Glycine (0–0 68)
	"		Valine (0–0 72)
	"		Alanine (0–0 51)
	"		Proline (0–0 63)
	"		Leucine (0–0 71)
	Arginine	–	Aspartic acid (0–0 49)
	"		Glutamic acid (0–0 57)
	"		Cysteine (0–0 52)
	"		Methionine (0–0 59)
	"		Phenylalanine (0–0 58)
	"		Glycine (0–0 68)
	"		Valine (0–0 62)
	"		Alanine (0–0.56)
	"		Proline (0–0.56)
	"		Leucine (0–0.75)

One or two drops of the test solution were spotted on the paper strips with thin capallaries. The papers were conditioned for 5 min. before being developed by the ascending technique. The ascent was 10 cm in all cases. The spots on the developed strips were detected

with 2% ninhydrin solution as usual.

The R_f values of 24 amino acids in different solvent systems on plain and impregnated papers (SPS) are shown in Fig. 1. Similar results were obtained on TPS papers. Separations achieved are summarized in Table 1. SPS papers were preferred over TPS papers because of the ease of availability of tin salts. All the amino acids have zero R_f value in acetone, benzene, ether and n-butanol on plain and impregnated papers. Hence they are not included in the figure.

As the results show the impregnated papers generally have a greater affinity for basic amino acids probably because of a strong binding force between the basic amino acids and the acidic exchange sites. Histidine, lysine, arginine and ornithine are fully retained on SPS papers. However, on TPS papers they move to some extent. Thorium, being baser than tin, might have produced a material possessing less active acid sites as compared to the material produced by tin. It is evident by the appreciable movement of the acidic and neutral amino acids on both the papers. Size of the molecule does not apparently affect the movement. Varshney *et al.*[10] have observed earlier that the acidic amino acids are completely retained on papers impregnated with an amphoteric material like hydrous zirconium oxide in acidic media which is obvious in view of the observations made in these studies. Nature of the solvent also appears to play an important role. It is observed that all the amino acids studied generally have a higher mobility in acids, phenols and water as compared to other solvents. However, methanol gives better results as in this solvent the spots are compact and the development time is greatly reduced.

The authors thank Professor A. U. Malik and Professor K. T. Nasim for providing research facilities and to the C.S.I.R., New Delhi, for financial assistance.

References

1. Alberti, G. & Grassini, G. (1960) *J. Chromatog.* 4423.
2. Qureshi, M. & Sharma, S. D. (1973) *Anal. Chem.* **45** : 1283.
3. Qureshi, M., Varshney, K. G., Gupta, M. P. & Gupta, S. P. (1977) *Chromatographia* **10** : 29.
4. Qureshi, M., Varshney, K. G. & Khan, F. (1973) *Sep. Sci.* **8** : 279.
5 Tuckerman, M M (1958) *Anal. Chem.* **30** : 231.
6. Knight, C. S. (1962) *J. Chromatog.* **8** : 205.
7. Varshney, K G., Anwar, S. & Khan, A.A. (1986) *Anal. Lett.* **19** : 543.
8 Singh, J. N., Rajeev & Tandon, S.N. (1977) *Ind. J. Chem.* **15B** : 581.
9. Varshney, K. G. & Premadas, A. (1981) *J. Liq. Chromatog.* **4** : 715.
10 Varshney, K. G., Sharma, U. & Rani, S. (1984) *J. Ind Chem Soc.* 61(3) : 220.

K. G. VARSHNEY, SHAHANA ANWAR and S. M. MAHESHWARI

Analytical Laboratories, Applied Chemistry Department, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh–202 002, India.

J inorg nucl Chem 1968 Vol 30 pp 3081 to 3090 Pergamon Press Printed in Great Britain

2.26 PREPARATION AND PROPERTIES OF STANNIC TUNGSTATE

MOHSIN QURESHI and K G VARSHNEY
Chemical Laboratories, Aligarh Muslim University, Aligarh, India

(*First received* 9 *October* 1967, *in revised form* 2 *April* 1968)

Abstract—Stannic tungstate gel (Sn W ratio 3 1) has been prepared by mixing 0 02 M aqueous solutions of stannic chloride and sodium tungstate in the volume ratio 2 1 Its ion exchange capacity is 0 57 meq/g Its chemical stability, K_d values and pH titration curves are also described

INTRODUCTION

SYNTHETIC inorganic ion exchangers based on tin[1–3] are highly selective, and several difficult and important analytical separations have been achieved on papers impregnated with stannic phosphate and stannic tungstate[2, 3] No systematic work has been reported on stannic tungstate, which was first prepared by Lotz[4] The present report summarizes the results of a study of its properties.

EXPERIMENTAL

Reagents Stannic chloride pentahydrate and sodium tungstate (B D H Analar) were used All other chemicals were of reagent grade

Apparatus Spectrophotometric studies were performed with a Bausch and Lomb spectronic 20 colorimeter pH measurements were made on a pH-meter of Electronic and Industrial Instruments Co Pvt Ltd, Hyderabad, India, and high-frequency titrations on a Sargent Oscillometer type V (E H Sargent & Co, Chicago), with a 100 ml cell Conductances were measured on a Philips Conductometric bridge, model PR 9500

Preparation of Stannic tungstate Stannic tungstate gel was prepared by mixing aqueous solutions of 0 02 M stannic chloride and 0 02 M sodium tungstate in the (molar) ratio 2 1 The gel was digested at room temperature for several hours, washed with water, filtered and dried at room temperature On immersion in water it broke down to small particles with cracking and slight evolution of heat For distribution studies the gel was broken down to the desired particle size and sized by sieving It was converted to the hydrogen form by immersion in dil HNO_3 for 24 hr, the acid being intermittently replaced, it was then washed several times with water till the pH of the washing water was 6 Finally it was filtered and dried in air

Properties The product is in the form of white, hard, semitransparent grannules suitable for column operation No change in colour or form was observed on heating with water The exchanger turned yellow when placed in HCl, but no change in colour was observed in H_2SO_4, HNO_3, $HClO_4$ or NaCl solutions

1 *Composition* 0 100 g of the exchanger was dissolved in 50 ml conc HCl, and the solution was diluted to 100 ml with distilled water Standard sodium molybdate solution (40 ml), containing 1000 ppm Mo, was added to it (tungsten is not quantitatively precipitated by α-Benzoinoxime in the absence of molybdenum[5]) It was verified experimentally that in the presence of molybdenum both tungsten

1 M Qureshi and S Z Qureshi, *J Chromat* 22, 198 (1966)
2 M Qureshi and J P Rawat, *J inorg nucl Chem* 30, 305 (1968)
3 M Qureshi, I Akhtar and K N Mathur, *Analyt Chem* 39, 1766 (1967)
4 J W Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol 11, p 792 Longmans, Green, London (1931)
5 G E F Lundell and J I Hoffman, *Outlines of Methods of Chemical Analysis*, p 121 Wiley, New York (1958)

and molybdenum are quantitatively precipitated as lead salts. The mixture was cooled to 5–10°C in an ice bath and the separation of tin from molybdenum along with tungsten was achieved by α-Benzoinoxime[6]. Molybdenum and tungsten were estimated as lead molybdate and lead tungstate[7]. The actual weight of tungsten was calculated by difference. Tin in the filtrate was reduced with lead and sulphuric acid and determined both iodometrically and oxidimetrically[8]; the results in both cases were the same. High-frequency titrations were performed with 2·0 ml 0·1 M sodium tungstate in the cell, adding 0·1 M aqueous stannic chloride solution from the burette. The results are shown in Fig. 1.

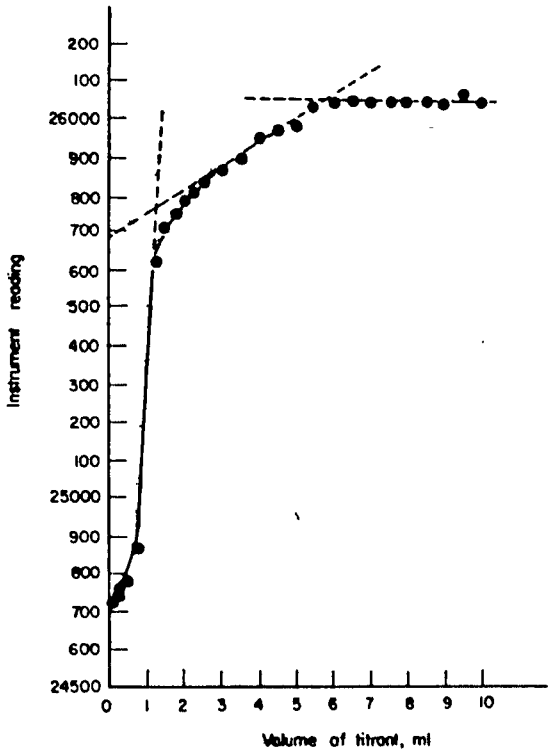


Fig. 1. High frequency titration of sodium tungstate against stannic chloride.

Conductometric titrations (Figs. 2 and 3) confirmed the high-frequency data.

2. *Ion exchange capacity.* The product is a cation exchanger, and its capacity was determined for uni- and bivalent cations by a standard method[9], with the results in table 1. The column was prepared in a glass tube of internal diameter 1 cm, and the flow rate was ~ 0·5–0·6 ml/min.

3. *Chemical stability.* In HNO_3, H_2SO_4, $HClO_4$, HCOOH, CH_3COOH and NH_4OH the exchanger remained unaffected even after 48 hr, but in HCl the particles turned yellow within 5 min. Detailed studies on the solubility of the exchanger were carried out, after first washing with hot water to remove any tin or tungsten adhering to the particles, by refluxing 500 mg with 50 ml of the required

6. H. Yagoda and H. A. Fales, *J. Am. chem. Soc.* 60, 640 (1938).
7. C. Sterling and W. P. Spuhr, *J. ind. Engng Chem. (Anal. Edn)* 12, 33 (1940).
8. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Volume 3, pp. 196, 320–22. Interscience, New York (1957).
9. O. Samuelson, *Dissn. tekn. Hogskolan, Stockholm* (1944).

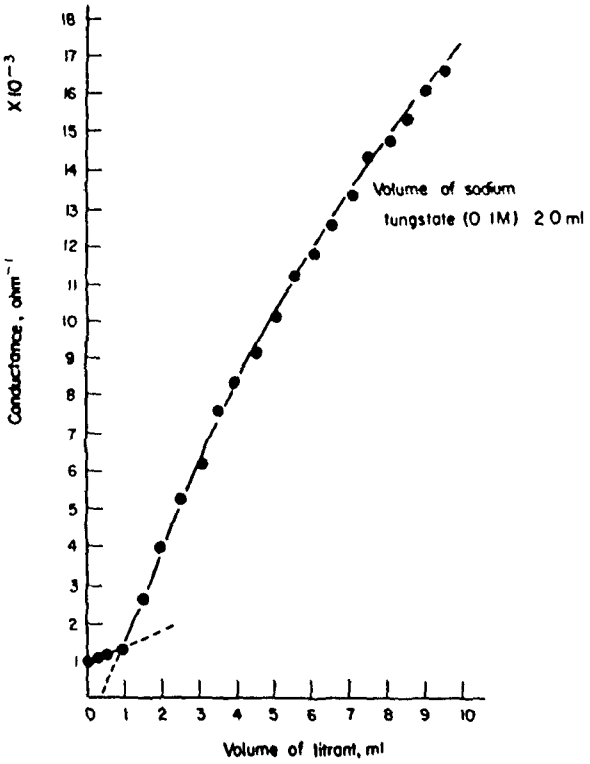


Fig. 2. Conductometric titration of sodium tungstate against stannic chloride

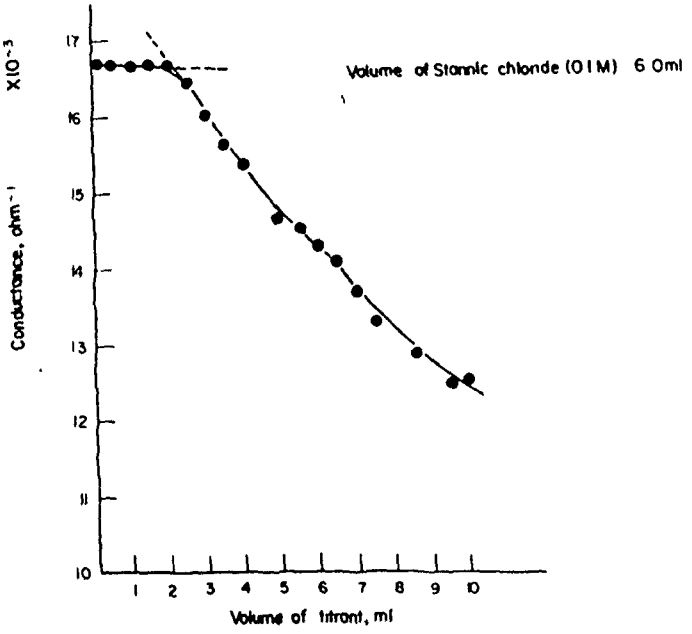


Fig. 3. Conductometric titration of stannic chloride against sodium tungstate.

Table 1. Ion exchange capacity of stannic tungstate

Metal ion	Capacity (meq/g dry resin)
Na^+	0·50
K^+	0·57
Mg^{++}	0·58
Sr^{++}	0·59

solution for 1 hr. After cooling, the solution was filtered and tungsten determined spectrophotometrically in the filtrate with thiocyanate[10] and tin with phenyl fluorone[11]. Tin only was determined after refluxing in distilled water and 8 M HNO_3 since in these cases no tungsten was found. The results are summarized in Table 2.

Table 2. Chemical stability of stannic tungstate

Serial No.	Solution	W dissolved (mg)	Sn dissolved (mg)
1.	Distilled water	0·00	0·065
2.	16 M HNO_3	7·25	—
3.	8 M HNO_3	0·00	0·27
4.	4 M HNO_3	0·00	—
5.	4·5 M H_2SO_4	22·50	—
6.	2 M H_2SO_4	7·75	—
7.	1 M H_2SO_4	4·26	—
8.	2·5 M HCl	16·00	—
9.	1 M HCl	14·00	—
10.	60% $HClO_4$	1·00	—
11.	10% $HClO_4$	1·00	—
12.	1 M Oxalic acid	Dissolved appreciably	—
13.	0·5 M Oxalic acid	Dissolved appreciably	—
14.	0·25 M Oxalic acid	255	—
15.	0·1 M Oxalic acid	125	—
16.	1 M NH_4OH	320	—
17.	0·5 M NH_4OH	Dissolved appreciably	—
18.	0·1 M NH_4OH	45	—
19.	1 M NaOH	Completely dissolved	—
20.	0·1 M NaOH	20	—
21.	0·01 M NaOH	20	—

4. *pH-titration curves.* The method of Topp and Pepper[12] was used; 90 ml of solution, containing different amounts of NaOH were added to 1 g of the exchanger. The pH was recorded after 3 days at constant temperature (±1°C), the solutions being shaken intermittently. 50 ml was withdrawn

10. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd revised Edn, pp. 886–890. Interscience, New York (1959).
11. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd revised Edn, pp. 862–865. Interscience, New York (1959).
12. N. E. Topp and K. W. Pepper, *J. chem. Soc.* 3299 (1949).

from each flask, a known volume of standard hydrochloric acid solution was added and the excess acid was back titrated. The experiment was repeated in the presence of sodium chloride keeping sodium ion concentration constant (0·1 M). The results are shown in Figs. 4 and 5, with a curve for stannic molybdate for comparison.

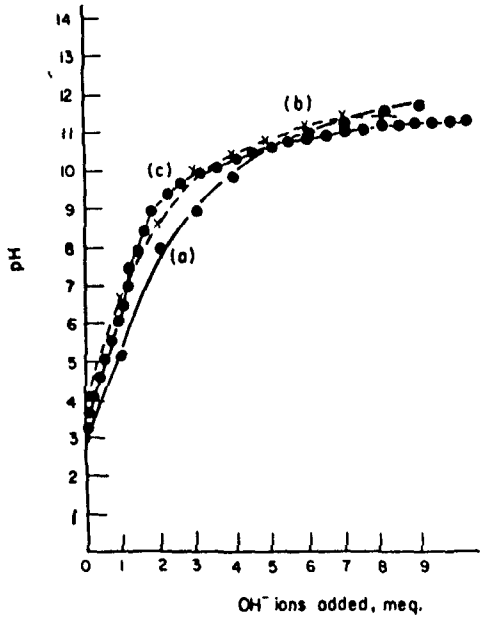


Fig. 4. pH-titration curve for stannic tungstate (OH^- ions added vs. pH). (a) In the presence of NaCl. (b) In the absence of NaCl. (c) For stannic molybdate.

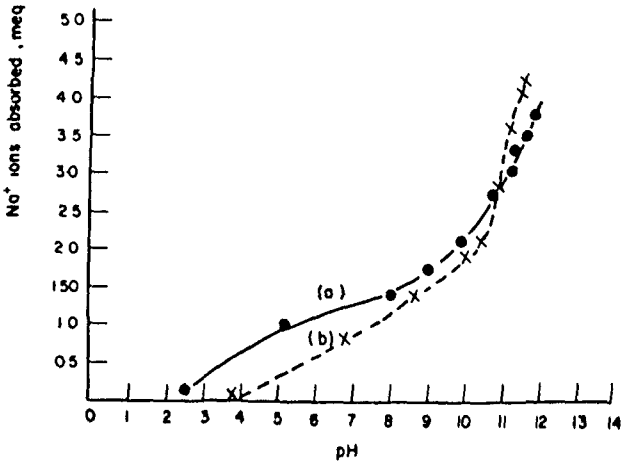


Fig. 5. pH-titration curve for stannic tungstate (pH vs. Na^+ ions absorbed). (a) In the presence of NaCl (b) In the absence of NaCl.

5. *Elution curve.* The optimum concentration of KNO_3 (100 ml) for complete elution of hydrogen ions from the exchanger was determined by using different concentrations of KNO_3 solution (Fig. 6), and the elution curve in Fig. 7 was obtained with KNO_3.

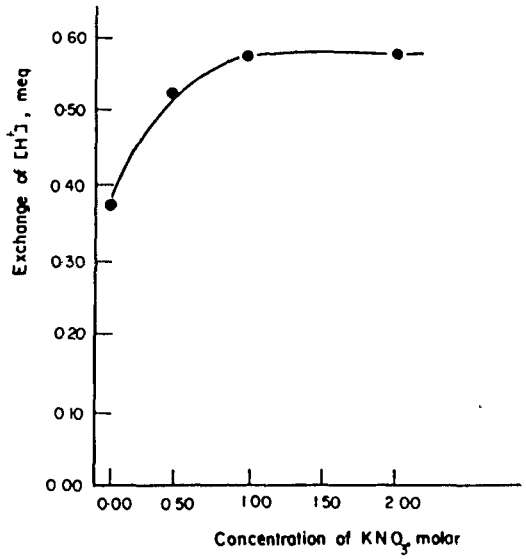


Fig. 6. Exchange capacity as a function of concentration.

6. *Distribution coefficients.* Distribution coefficients were determined with 0·5 g of exchanger (H-form, 50–100 mesh), 0·5 ml of the cation solution and 49·5 ml of demineralized water; the concentration of the cation was adjusted so that the concentration of the cation did not exceed 3 per cent of the total capacity per gram of the exchanger. After equilibrating at 25 ± 1°C for 6 hr with occasional shaking, 40 ml of solution were then withdrawn and titrated against standard EDTA solution[13]. The results are summarized in Table 3.

Table 3. Distribution coefficients for metal ions on stannic tungstate

Metal ion	K_d(ml g^{-1})
Pb(II)	150·0
Mn(II)	114·6
Zn(II)	41·4
Mg(II)	94·4
Cd(II)	77·8
Cu(II)	116·0
Ni(III)	136·8
Co(II)	586·0
Ba(II)	156·0
Sr(II)	114·0

13. C. N. Reilley, R. W. Schmid and F. S. Sadek, *J. chem. Educ.* **36**, 555 (1959).

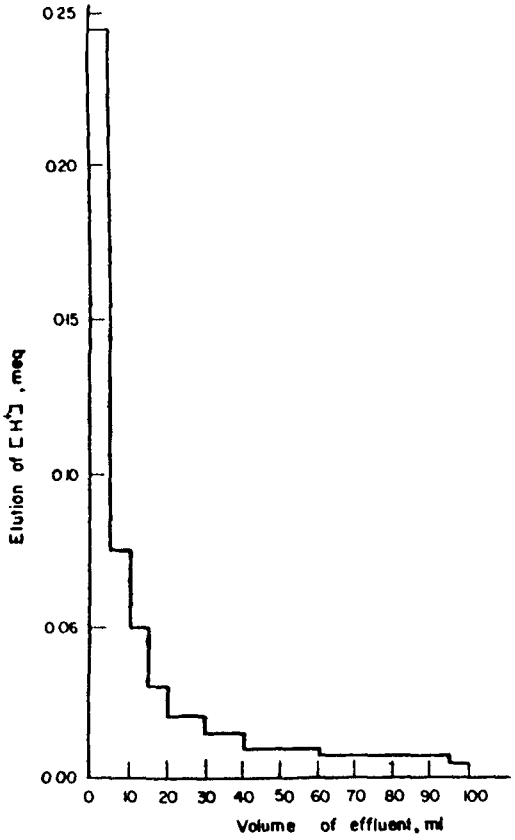


Fig. 7. Elution curve for stannic tungstate.

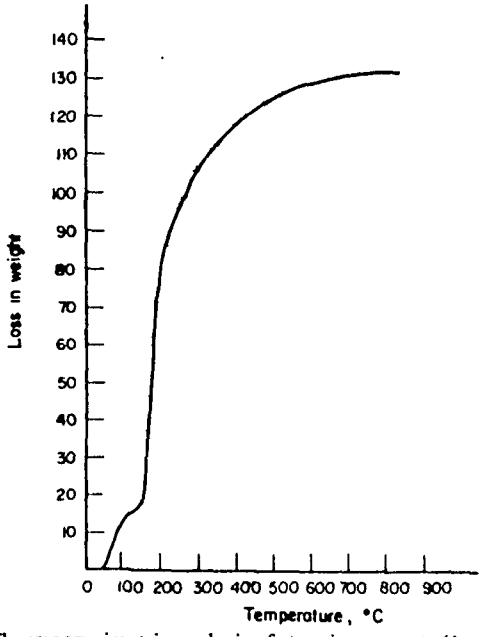


Fig. 8. Thermogravimetric analysis of stannic tungstate (1g sample).

7. *Thermogravimetry.* The results of thermogravimetric analysis of the ion exchanger are given in Fig. 8. To determine the effect of heat on the colour and the capacity of stannic tungstate, 1 g samples were heated at temperatures from 100° to 800°C in a muffle furnace for 1 hr, with the results shown in Table 4.

Table 4. Effect of heating on Stannic tungstate

Temperature (°C)	Colour of the beads	Capacity (meq./g)
Room temp.	White	0·57
100	White	0·13
200	White	0·10
300	Very light yellow	0·10
400	Light brown	0·10
500	Brown	0·10
600	Dark brown	0·10
700	Blackish brown	0·10
800	Blackish	0·10

DISCUSSION

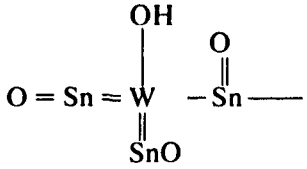
The observed K_d values show that stannic tungstate is a useful ion exchanger and many interesting separations are possible, as has been demonstrated by paper chromatographic studies in our laboratories[1, 3]. Some corresponding column separations may also be possible. Values of K_d for Ba^{++}, Sr^{++}, Mg^{++} are in the same order as for stannic molybdate[2] and zirconium phosphate[14]. R_f values of metal ions in 0·1 M $HClO_4$ are also in qualitative agreement with K_d values, provided we consider ions belonging to the same group in the periodic table (cf. Table 5).

Table 5. Comparison of K_d values with R_f values on Stannic tungstate papers

Serial No.	Cation	K_d	R_f in 0·1 M $HClO_4$
1.	Pb(II)	150·0	0·07
2.	Mn(II)	114·6	0·23
3.	Zn(II)	41·4	0·53
4.	Mg(II)	94·4	0·75
5.	Cd(II)	77·8	0·58
6.	Ni(II)	116·0	0·87
7.	Cu(II)	136·8	0·55–0·00
8.	Co(II)	586·0	0·28
9.	Ba(II)	156·0	0·36
10.	Sr(II)	114·0	0·41

14. C. B. Amphlett, *Inorganic Ion Exchangers.* Elsevier, Amsterdam (1964).

The composition of stannic tungstate was found to be Sn:W = 3:1, and the high frequency titrations confirm this conclusion. When sodium tungstate is added to stannic chloride in the titration cell no end-point is obtained, since in this case the conductivity is very high, owing to the low pH of the solution. However, when sodium tungstate is taken in the cell two breaks are obtained corresponding to Sn:W ratios of 1:2 and 3:1; similar ratios were obtained conductimetrically. The precipitate which is first formed corresponds to normal stannic tungstate, which changes on adding more stannic chloride to the tungstate which is actually isolated. The following structure is tentatively postulated. Since only one inflection is observed in the pH-titration curve, it appears that the exchanger behaves as a monofunctional acid.



Stannic tungstate does not give a yellow colour with HNO_3 or with sodium chloride alone. However, the yellow colour observed when they are mixed shows that some complex formation occurs with HCl, but further study is required. The pH-titration curves show that initially there is some hydrolysis (pH = 4). On titration with NaOH alone there is a more rapid increase in pH than in the presence of NaCl. The addition of NaCl releases some of the hydrogen ions from the exchanger, thus decreasing the pH. A plot of sodium ions absorbed versus pH (Fig. 5) resembles curves obtained by Topp and Pepper for monofunctional weak acid cation exchangers. Figure 6 shows that the capacity is strongly dependent on $[K^+]$, and becomes constant at ~ 1 M$[K^+]$. The elution curve (Fig. 7) shows that almost all the H^+ ions are released in the first 25 ml of the eluent. In both these aspects the behaviour of stannic tungstate resembles closely that of stannic molybdate. The ion exchange capacity of stannic tungstate is lower than that of stannic phosphate[3] and stannic molybdate[2], but this disadvantage is compensated by the fact that stannic tungstate is much more stable than stannic molybdate (table 6).

Table 6. Solubilities of stannic tungstate, molybdate and phosphate in water and 6 N HNO_3

Solvent	Stannic tungstate		Stannic molybdate		Stannic phosphate[15]	
	Sn (mg)	W (mg)	Sn (mg)	Mo (mg)	Sn (mg)	P_2O_5 (mg)
Distilled water	0·06	0·00	3·50	3·31	0·03	6·5
6 N HNO_3	0·27	0·00	9·45	20·25	1·5	3·4

15. Y. Inoue, *J. inorg. nucl. Chem.* **26**, 2241 (1964).

On heating the exchanger to 100°C there is some loss in weight and the capacity decreases to 0·13 meq./g. Significant structural changes must take place over this temperature range, and condensation may occur with removal of water. On heating to 200°C there is a loss in weight but the decrease in capacity is very small, and the latter remains constant up to 800°C. The weight loss is negligible above 600°C (Fig. 8).

Acknowledgements—The authors are grateful to Professor A. R. Kidwai for research facilities. Financial assistance to K. G. Varshney from the C.S.I.R. (India) is gratefully acknowledged. Mr. Irshad Masood (C.B.R.I., Roorkee, India) is thanked for T.G.A. work.

2.27

Cation Chromatography on Stannic Tungstate Papers: Quantitative Separation of Vanadium from Iron, Titanium, Zirconium and Thorium

216

M. Qureshi / K. G. Varshney

Chemistry Section, Z. H. College of Engineering and Technology, Aligarh Muslim University, Aligarh, India

M. P. Gupta / S. P. Gupta

Chemistry Department, D.N.College, Meerut, India

Summary

A systematic study of the chromatography of metal ions on stannic tungstate papers has been performed using acetone-HNO_3-H_2O systems. The effect of mole fractions of acetone, HNO_3 and H_2O on the R_f values of the metal ions has been discussed in detail and a relationship between R_f and mole fraction (X) of the solvent has been obtained as $R_f = mX + C$. The usefulness of the study has been demonstrated by the specific extraction of titanium and thorium in HNO_3:H_2O (1:2) and HNO_3:acetone:H_2O (1:6:1) systems. In addition, some binary and ternary separations of metal ions have also been achieved on these papers.

Introduction

Chromatography of metal ions on papers impregnated with salts of heteropolyacids was introduced by *G. Alberti* and coworkers [1] in 1960 who first separated alkali metals on ammonium molybdophosphate papers with 0.1 mol dm^{-3} and 0.2 mol dm^{-3} HNO_3 as solvents. A number of papers have been published since by workers from other laboratories [2–10]. *Qureshi* and *Qureshi* [11] first studied in 1966 the behaviour of 21 cations and 2 anions on stannic phosphate papers with HCl and $HClO_4$ as developers. The mixed solvent systems have shown very attractive possibilities on ion-exchange columns. However, they have not been adequately tested on ion-exchange papers. *Zhu Jun Zhang* and coworkers [12, 13] were the first to separate Li, Na, K, Rb and Cs on ammonium molybdophosphate and ammonium tungstophosphate papers using aqueous ethanolic 0.6 mol dm^{-3} NH_4NO_3 – 0.1 mol dm^{-3} HNO_3 and 0.4 mol dm^{-3} NH_4NO_3 – 0.1 mol dm^{-3} HNO_3 – methanol systems respectively. Stannic tungstate was synthesized as an inorganic ion-exchange material in these laboratories [14] and subsequent work was done on papers impregnated with this material [15, 16], using mixed solvent systems.

It was noticed in these studies that stannic tungstate papers, when developed with the mixed solvent systems, exhibit the possibility of a number of difficult separations and some were actually achieved. A systematic study in this direction was therefore, warranted. The present work summarizes our efforts to use, successfully, acetone – HNO_3 – water systems in varying ratios and some interesting results have been achieved. Nitric acid was selected as it is a non-complexing agent and hence the mechanism of separation is easier to study and also because inorganic ion-exchangers are very stable in this system. Acetone was selected because it does not solvate ions significantly and hence the discussion of mechanism is simpler.

Experimental

Cations Studied: The oxidation numbers of the metals used were as follows, unless otherwise stated:

Ag(I), Tl(I), Cu(II), Cd(II), Pb(II), Bi(III), Hg(II), Fe(III), Al(III), Cr(III), La(III), Ti(III), Co(II), Ni(II), Mn(II), Zn(II), Th(IV), Ce(IV), ZrO(IV), VO_2(III), UO_2(VI), Se(IV), In(III), Sm(III), Y(III), Pr(III), Nd(III), Gd(III), Dy(III), As(III), Sb(III), Be(II).

Apparatus: Chromatography was performed on 15 × 3.0 cm. Whatman No. 1 paper strips in glass jars of 21 × 5 cm.

Reagents: A.R. grade chemicals and reagents were used.

Preparation of Ion-Exchange Papers:

The paper strips were first impregnated in an aqueous 0.2 mol dm^{-3} stannic chloride for 3–5 sec and dried for 15 min on filter paper to remove excess reagent. These strips were then treated with aqueous 0.2 mol dm^{-3} sodium tungstate for 15 sec and allowed to dry over filter paper at room temperature. The dried strips were washed with distilled water and placed on filter sheets again. When dried they were used as such.

Test Solutions and Detectors:

These were prepared and used as described earlier [15]. Titanium was, however, prepared from a concentrated solution of titanous sulphate by diluting it with 3.6 mol dm^{-3} H_2SO_4, and vanadium by dissolving V_2O_5 in H_2SO_4 and diluting with water to 0.1 mol dm^{-3}.

Procedure

One or two drops of the test solution were spotted on the paper strips with thin capillaries The papers were conditioned for 15 min and then the solvent was allowed to ascend 10 cm in all cases and spots detected as usual. R_f values of leading front (R_L) and of the tailing front (R_T) were measured and reported as ($R_L - R_T$) in the paranthesis

Results

33 cations were chromatographed on papers impregnated with stannic tungstate in the following thirty solvent systems.

(a) 15 solvent systems containing HNO_3 : acetone : H_2O in the following proportions:
(1) 1.1.1 (2) 1:1:2 (3) 1:1.3 (4) 1:1:4 (5) 1:1:5 (6) 1:1:6 (7) 1:2:1 (8) 1:3:1 (9) 1:4:1 (10) 1:5:1 (11) 1.6:1 (12) 2:1:1 (13) 3:1:1 (14) 4:1:1 (15) 5.1.1 .

(b) 9 HNO_3 systems of the following concentrations: 8, 6, 4, 0 1, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} mol dm^{-3}.

(c) 6 KNO_3 systems of the following concentrations: 1, 0.1, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} mol dm^{-3}.

Some important and difficult separations, seemed possible on the basis of R_f values, were actually effected as reported in Table I For the separation of one metal ion from numerous others, synthetic mixtures were prepared. A drop of this mixture was chromatographed as usual. Quantitative separation of vanadium from iron, titanium, zirconium and thorium has been summarized in Table II. All these separations took 35 40 min.

Diskussion

A plot of R_f values versus mole fraction (X) gives some interesting results We will consider these plots as R_f vs $X_{acetone}$, R_f vs X_{HNO_3} and R_f vs X_{H_2O} where X stands for the mole fraction

Effect of mole fraction of acetone on R_f values

Figs. 1a and 1b have been plotted for systems 1, 7, 8, 9, 10 and 11 In all these systems the mole ratio of water and nitric acid remains constant. Under these circumstances, good straight lines are obtained which are in almost all cases parallel to one another if we consider only the unimpregnated papers. It is surprising to note that even though the R_f varies from 0.1 - 0 9 there is still no effect of (i) charge (ii) size or (iii) nature of the cation. Thus the lines for Co, Cd, Cu, Zn, Ni and Mn all have the same slope. The decrease in R_f with increase in mole fraction of acetone is due to a decrease in the number of hydrogen ions competing for the exchange sites. Thus, it follows that when the aqueous and non-aqueous solvents are both non-complexing and the HNO_3: water ratio remains constant, the R_f is almost always dependent on the number of H^+ ions competing for the exchange sites. When we consider the impregnated papers then in most cases lines parallel to those for plain papers are obtained with R_f values slightly less. This is because stannic tungstate offers a large number of exchange sites However, since tungstic acid is a weak acid it does not ionize significantly in the presence of nitric acid hence the number of exchange sites is not radically altered on impregnation and we observe only a slight difference in R_f values on impregnated and plain papers. The R_f values of Tl, SeO_3^{2-}, Tl, Pb, Be, and V on plain papers differ considerably from those on impregnated papers because these ions interact strongly either with the cation or with the anion of the exchanger. Be is, however, different from the rest of cations in that its slope is larger on impregnated paper than on plain paper

Table I. Separations achieved on stannic tungstate papers

S.No.	Solvent System	Separations
1.	HNO_3: acetone : H_2O (1:1:1)	ZrO (0.08–0.00) – La (0 85–0.65) ZrO (0.08–0.00) – Th (0 65–0 37) Se (0.12–0.00) – Tl (0.57–0.45) Se (0.12–0.00) – Cu (0 89–0 62) Tl (0.47 - 0.36) – Hg (0 85–0 65) Sb (0.27 - 0.00) – Hg (0 95 0 70) Sb (0.15–0.00) – Cd (0.80–0 60) Hg_2^{2+} (0.10–0 00) – Tl (0.52–0.32) – UO_2 (0.89 - 0 65)
2.	HNO_3: acetone : H_2O (1:2:1)	ZrO (0.07–0.00) – Ce (0.62–0.47) – Hg (1.0–0.80) ZrO (0.05–0.00) – Pb (0.42–0.20) – Hg (1.0–0.82) ZrO (0.08–0.00) – Rare earths (0.72–0.47) Ag (0.08 - 0.00) – Pb (0.45–0.25) – Th (0.78–0.62) As (0.20–0 00) – Cd (0.65–0.37) – Hg (1.00 - 0.80)
3.	HNO_3: acetone : H_2O (1:3:1)	Ti (0 15–0.00) – Th (0.90–0 80) Se (0.10–0.00) – Zn (0.54–0 30)
4.	HNO_3: acetone : H_2O (1:4:1)	Cu (0.45–0.18) – Bi (0.82 - 0 62) Tl (0.12–0.00) – Be (0.68 - 0.46) Fe (0.12–0.00) – Be (0.70–0.50) Ti (0.13–0.00) – Cd (0.50–0 28)
5.	HNO_3: acetone : H_2O (1:5:1)	Ag (0.16–0.00) – Bi (0.83–0 48) Fe (0.19–0.00) – UO_2 (0 90 - 0 68) UO_2 (0.93–0.70) from 28 cations (Bi, Th, Hg, and Sb interfere)
6.	HNO_3: acetone : H_2O (1:6:1)	Pb (0.14–0 09) – Bi (0.97 0 60) As (0.28 -0.00) – Sb (0.80–0 60) Th (0.80 - 0.77) from 28 cations (Bi, UO_2, Hg and Sb interfere)
7.	HNO_3: acetone : H_2O (2.1:1)	Ag (0.05–0.00) – Cd (0.90–0 60) As (0.20–0.00) – Cd (0.90–0 60) ZrO (0.25–0.00) – Y (0.95–0 60) Se (0.16–0.00) from 26 cations (Ti, Fe, As, Ag, ZrO, Hg_2^{2+} interfere) Ag (0.10–0.00) from 26 cations (Ti, Fe, As, Se, ZrO, Hg_2^{2+} interfere)
8.	HNO_3: acetone : H_2O (3.1:1)	Ag (0.00) – Mn (0.86–0 66) Ti (0.18 0 00) - Rare earths (0.90 0.60)
9.	HNO_3: acetone : H_2O (1.1:2)	Se (0.17–0 00) from 24 cations (Ti, Fe, ZrO, Ag, Sb, Bi, Hg_2^{2+} interfere) ZrO (0.10–0.00) from 24 cations (Ti, Fe, Se, Ag, Sb, Bi, Hg_2^{2+} interfere)

Note: numbers in parentheses in Separations column = ($R_L - R_T$) – see text.

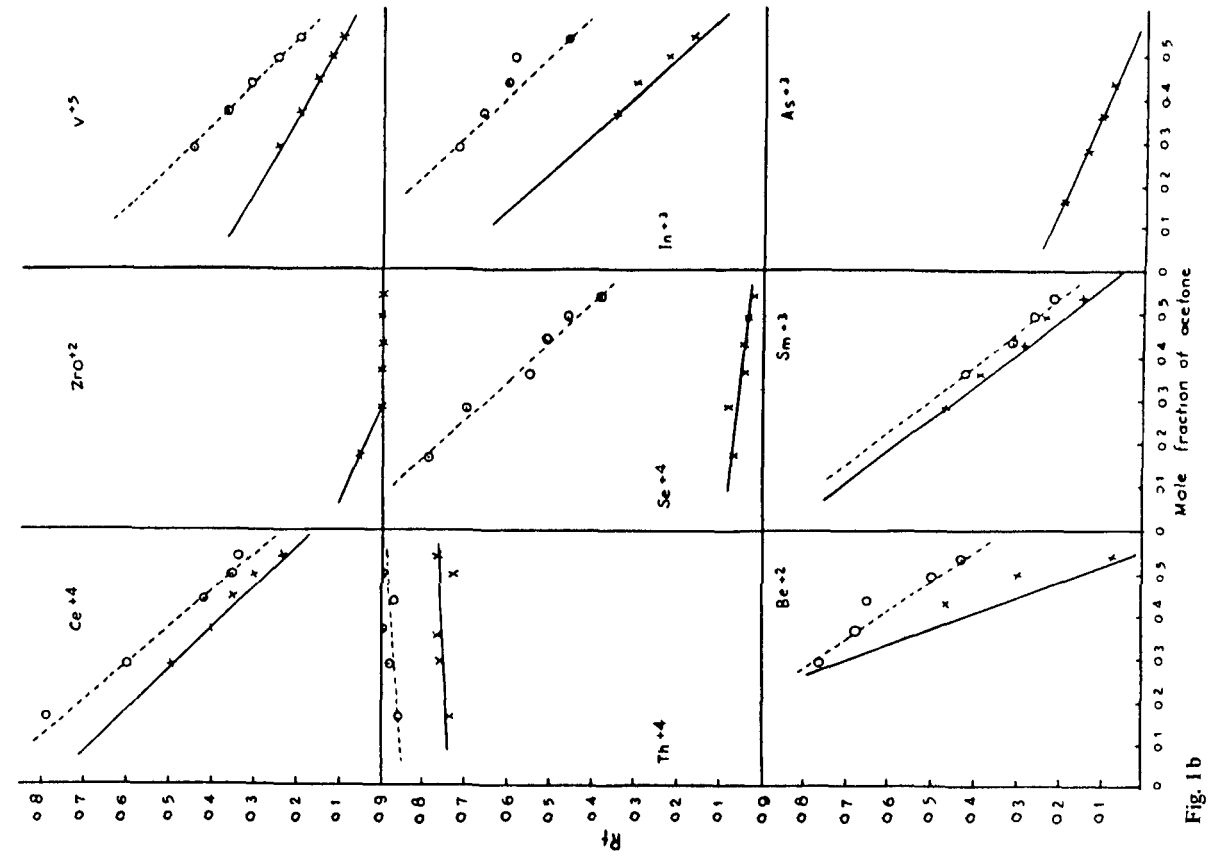


Fig. 1b

● R_f vs mole fraction of acetone

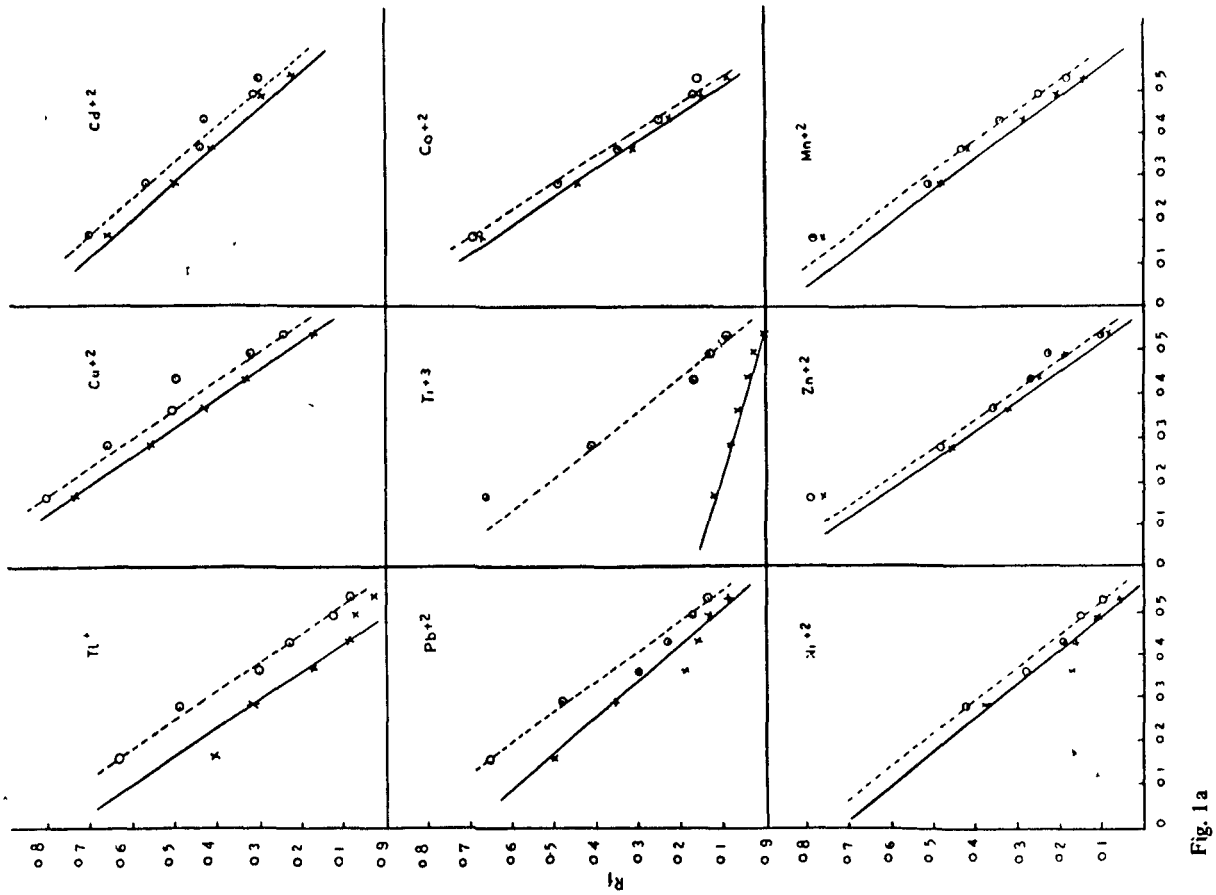


Fig. 1a

● R_f vs mole fraction of acetone

Table II. Quantitative separation of vanadium from Fe, Ti, ZrO and Th on stannic tungstate papers in 1.0 mol dm^{-3} HNO_3

Impuritiy added	Vanadium applied (μg)	Vanadium found (μg)	% error
Fe	100	102	+ 2
	100	103	+ 3
Ti	100	105	+ 5
	100	103	+ 3
ZrO	100	100	0
	100	102	+ 2
Th	100	105	+ 5
	100	104	+ 4

whereas the reverse is true for Ti, SeO_3^{2-}, Tl, Pb and V. The change in the nature of the slope of Be is due to the fact that Be^{2+} is a small and polarising ion. In low acetone concentrations its R_f values on the plain and the impregnated papers are almost the same. At high acetone concentrations the difference is enhanced for the same reason. In the case of Zr the R_f is very small probably due to precipitation or hydrolysis. Th has a very high R_f value perhaps because thorium nitrate is very soluble in acetone [11] and water in addition to its high complexing nature in nitrate system. Another point worth noting is that as the nitric acid concentration is high the exchanger is not ionized and mostly acts as an adsorbent. Thus in the case of Co, Ri (R_f on plain papers – R_f on impregnated papers) is very small. Since R_f is very small in most cases probably the same mechanism is applicable in the two types of papers. Further, whenever, there is any significant departure (selenite, vanadium) this is probably a result of chemical rather than of physical interaction.

Effect of the mole fraction of HNO_3 on R_f values

These curves (Figs. 2a and 2b) are also very revealing. R_f values generally increase linearly with the mole fraction of HNO_3 except for Th and In. In this case we have plotted the data for systems 1, 12, 13, 14 and 15, where the water-acetone mole ratio remains the same while the HNO_3 acid mole fraction is being continuously increased. The increased R_f is now easily explained in terms of the increase in the number of H^+ ions competing with the cations for the exchange site. Indium is probably an exception in which the R_f value is not significantly affected by the increase in the mole fraction of HNO_3. The R_f of Th decreases with an increase in the mole fraction of HNO_3 because it means total decrease in the acetone concentration and as explained earlier Th is highly soluble in acetone.

Effect of the mole fraction of water on R_f values

In this case we have plotted R_f values for systems 1–6 where the mole ratio of acetone and nitric acid is fixed while the mole fraction of water is increased. The increase in the mole fraction of water means an increase in the ionization of nitric acid and therefore, the R_f values increase linearly with the mole fraction of water. The exceptions are UO_2 and Pb. In the case of uranyl, with an increase in the mole fraction of water there is a greater formation of the insoluble uranyl tungstate resulting in a decrease in the R_f value. A similar explanation is true for lead. The plots of R_f vs X_{H_2O} show much greater variation than the plots of R_f vs X_{HNO_3} because in the case of water plots the R_f is almost always greater than 0.5 and hence it leads to greater dispersion.

Lederer had suggested that for ion-exchange papers the relation $R_M = n\,pH + constant$, where n is the charge on the ion, holds good. We, however, find that $R_f = mX + C$ where X represents the mole fraction of acetone, HNO_3 or water. In other words in the three component systems acetone : HNO_3 : water the R_f depends on the mole fraction of any one component provided that the mole ratio of the other two component remains constant. The values of m and C for various cations are given in Table III. It will be interesting to investigate the same systems with lower HNO_3 concentration. Then it is possible that the effect of the variables mentioned above i.e. charge, size and nature of the cations may become important. It will also be interesting to correlate the R_f of ions like SeO_3^{2-} and VO^{2+} with the amount of impregnated material on the paper. The R_f of SeO_3^{2-} may than become a pointer to the degree of impregnation of the paper.

The results in acetone : water : HNO_3 systems can be corroborated by the complementary studies in water HNO_3 system. Here for typical cases of Co and Pb the R_f is maximum at pH = 2. As the pH decreases the number of ionized sites on the impregnated paper decreases and the impregnated paper behaves as an unimpregnated paper. Thus $R_f = 0$ for $[HNO_3] \geqslant 2$ mol dm^{-3}. In the case of the selenite ion the R_f is as large as in the acetone system due to conventional chemical interaction. The behaviour of Be is now more as in this case the departure was due to the presence of acetone.

Similarly the exceptional behaviour of Th was explained in terms of its high solubility in acetone. In the absence of acetone it becomes normal.

Since V and SeO_3^{2-} interact strongly with the ion-exchange material the impregnated papers become very selective for these ions. The utility of these papers has been demonstrated by the quantitative separation of V from Fe, Ti, Zr and Th (Table II).

When the stannic tungstate papers are dipped in KNO_3 solution the papers are obtained in the K^+ form. When the KNO_3 solvent systems with concentrations of KNO_3 from 1 to 10^{-5} mol dm^{-3} were tried on these papers it was observed that the R_f values were suppressed by this treatment. The exchanger in the K^+ form is ionized more and hence there is a large increase in the number of exchange sites and the R_f values decrease. Only Zn and Al have a significant R_f (1.0–0.80) on these papers and hence they can be separated from many other cations

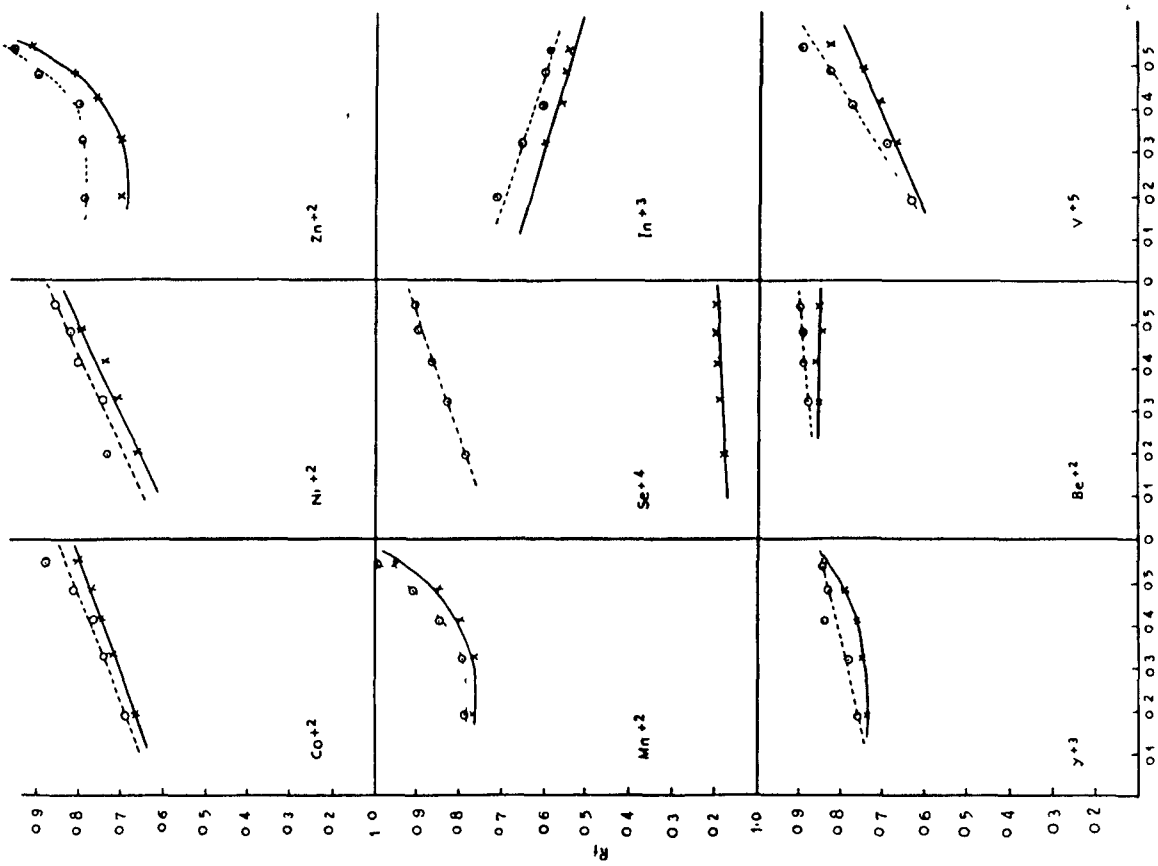


Fig. 2b

● R_f vs mole fraction of HNO_3

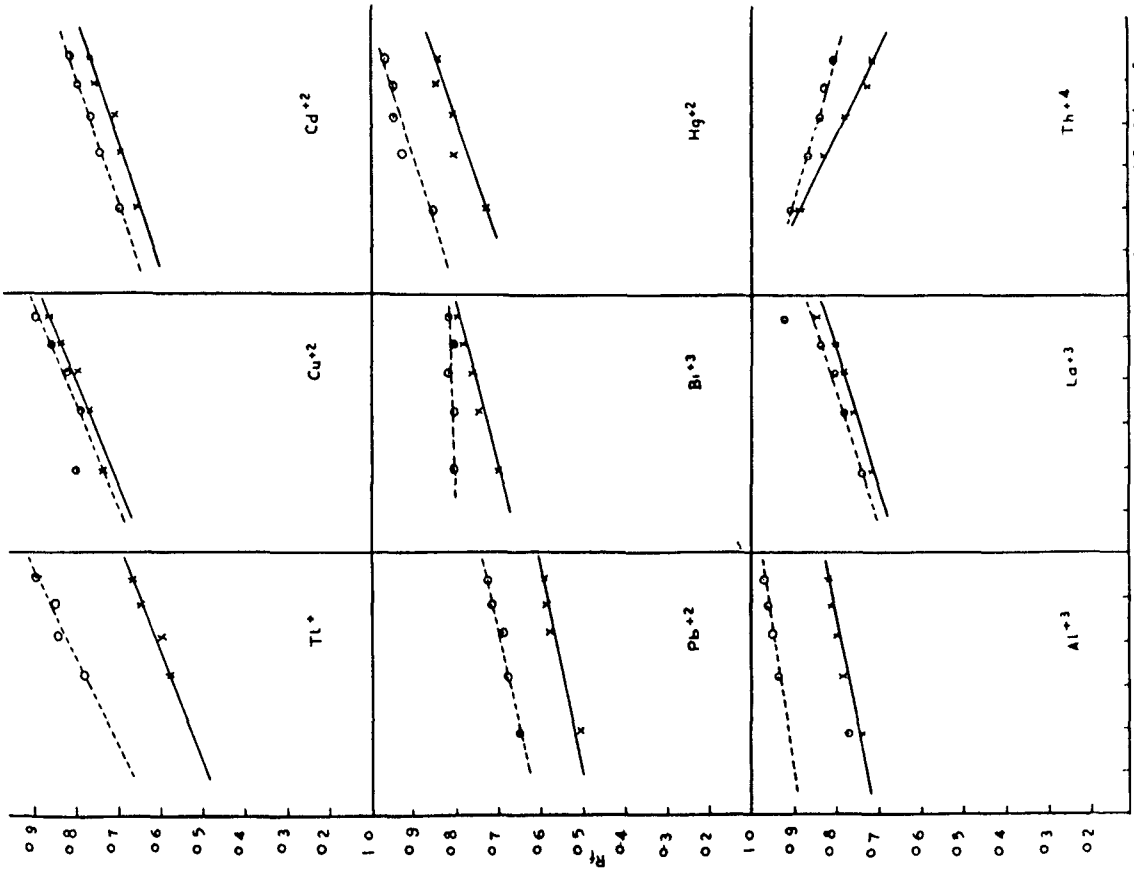


Fig. 2a

● R_f vs mole fraction of HNO_3

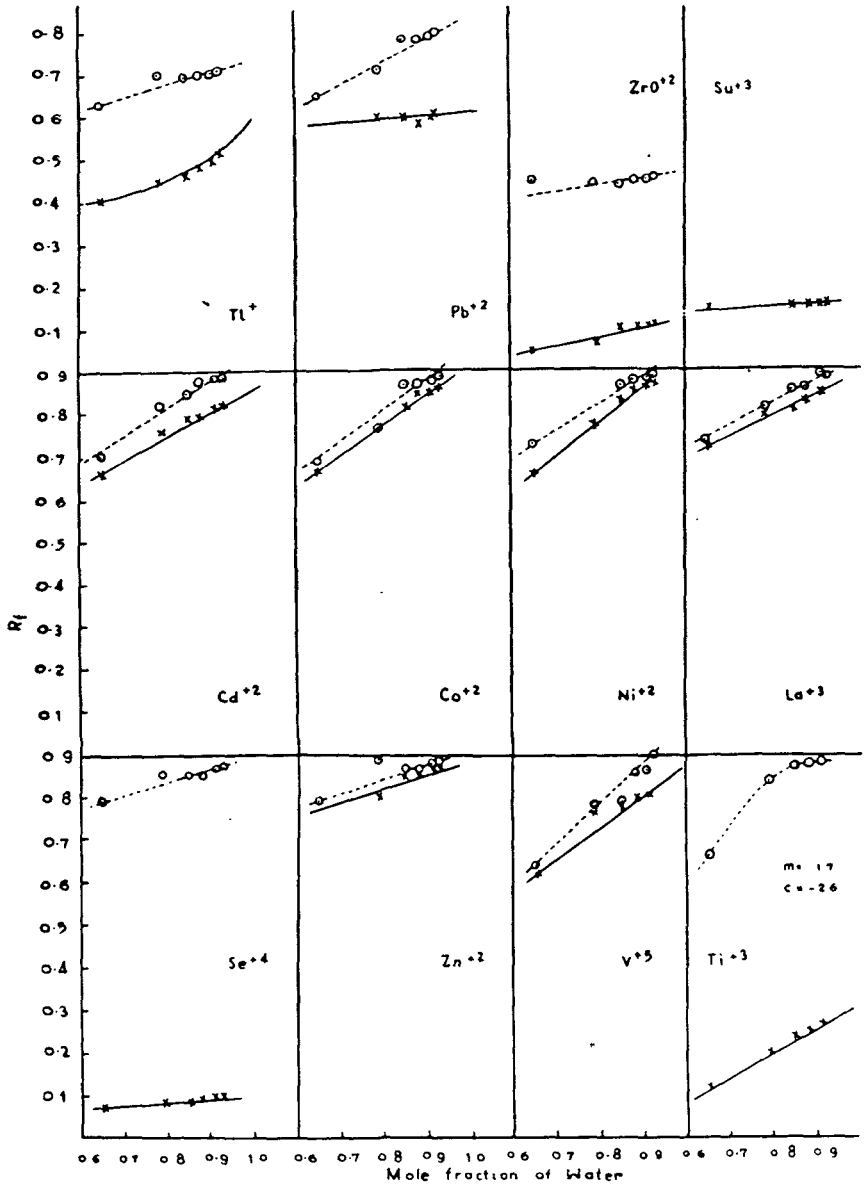


Fig. 3a

● R_f vs mole fraction of water

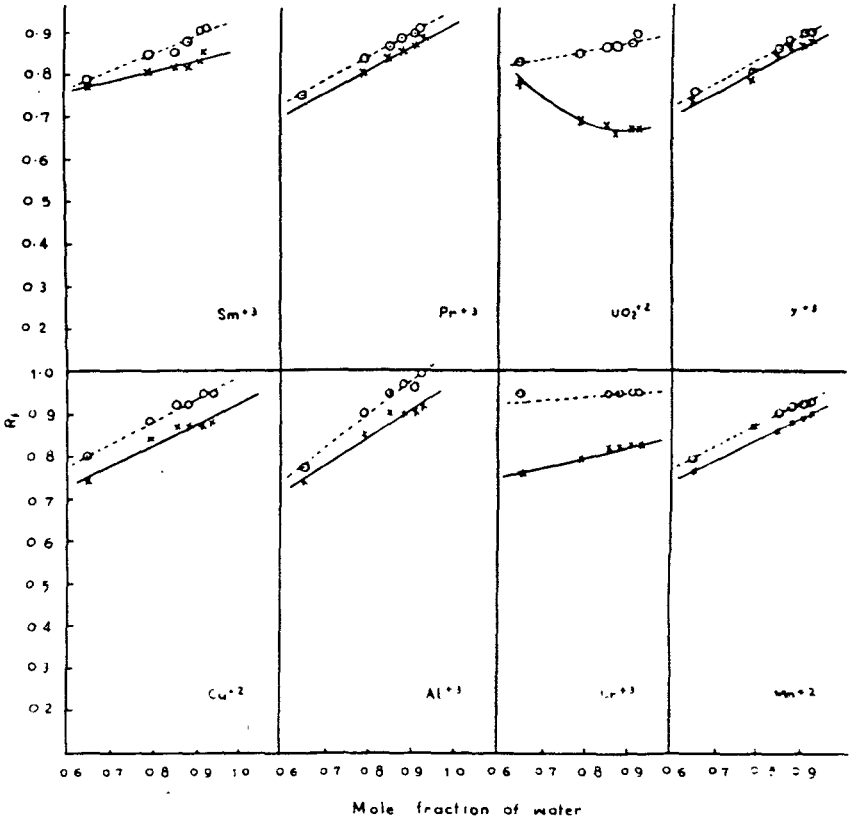


Fig. 3b

● R_f vs mole fraction of water

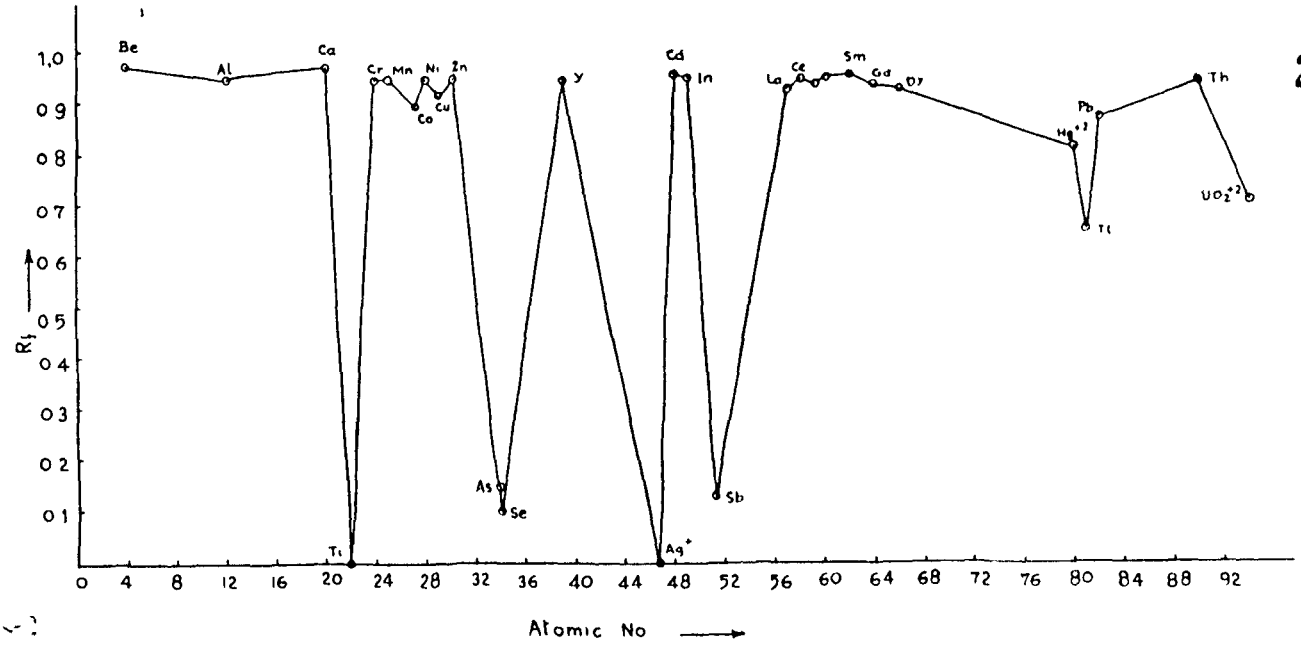


Fig. 4

R_f vs atomic number of metal ions on impregnated papers in solvent system HNO_3 – water (1 2)

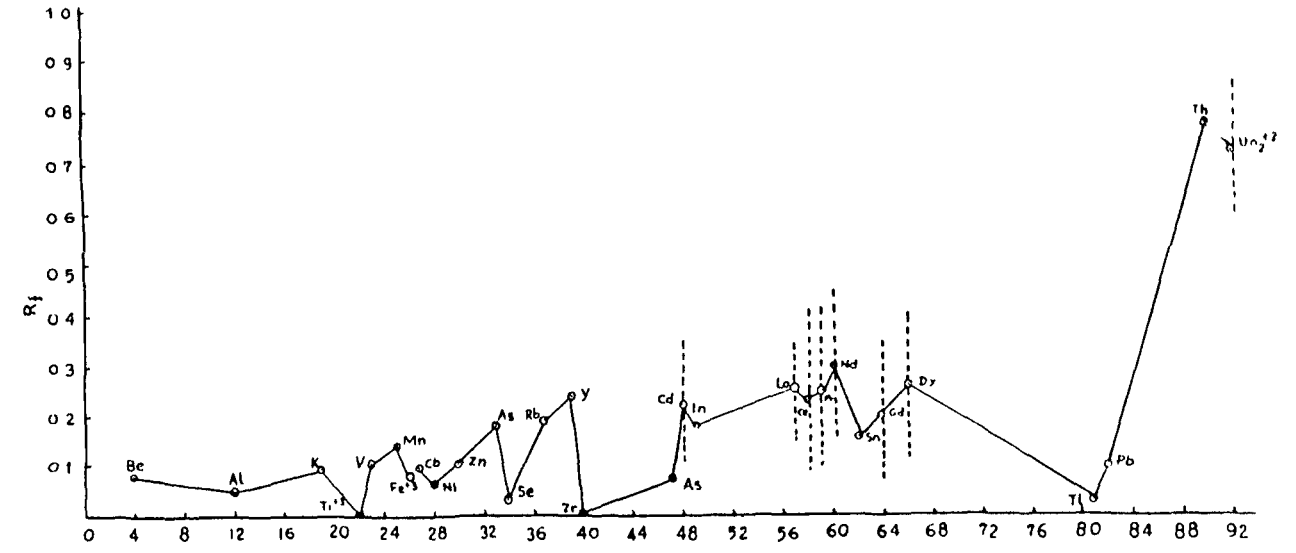


Fig. 5

R_f vs atomic number of metal ions on impregnated papers in solvent system HNO_3 – acetone – water (1 6 1)

using 1 mol dm^{-3} KNO_3 as the mobile phase These cations have thus been separated from 17 others

Metals which interfere in these separations are Cu, Cd, Bi, Co, Ni, Mn, Be and lanthanons

From 30 solvent systems used in these studies the solvent systems HNO_3 – water (1.2) and HNO_3 – acetone – water (1.6 1) are useful for almost specific extractions of titanium and thorium respectively (Figs 4 and 5)

Acknowledgement

The authors are thankful to Dr *K D Agarwal* and Dr *P C Gupta* for research facilities and encouragement

Table III. Values of m and C in $R_f = mX + C$ for metal ions on plain and impregnated papers in solvent systems containing varying mole fractions of acetone, HNO_3 and water

Cation	Varying acetone mole fraction				Varying HNO_3 mole fraction				Varying water mole fraction			
	Impregnated paper		Plain paper		Impregnated paper		Plain paper		Impregnated paper		Plain paper	
	m	C	m	C	m	C	m	C	m	C	m	C
Tl	-1.50	0.75	1.60	0.90	0.40	0.45	0.6	0.61	-		0.20	0.51
Cu	-1.50	0.98	-1.40	1.02	0.50	0.62	0.5	0.65	0.40	0.50	0.40	0.55
Cd	-1.20	0.84	1.20	0.89	0.40	0.58	0.4	0.63	0.50	0.34	0.60	0.33
Pb	-1.20	0.71	-1.40	0.87	0.30	0.47	0.03	0.60	0.10	0.51	0.50	0.32
Ti	-0.30	0.16	-1.40	0.78	-	-	-	-	0.60	0.28	-	
Co	-1.50	0.80	-1.60	0.96	0.40	0.59	0.40	0.61	0.70	0.21	0.70	0.25
Ni	-1.30	0.73	-1.40	0.80	0.50	0.56	0.50	0.60	0.80	0.14	0.60	0.34
Zn	-1.40	0.85	-1.40	0.90	-	-	-	-	0.30	0.58	0.30	0.60
Mn	1.30	0.85	1.40	0.93	-				0.50	0.44	0.50	0.47
Ce	-1.10	0.78	1.20	0.94	-							
ZrO	-0.30	0.11	-	-	-	-	-	-	0.20	0.80	0.20	0.28
V	-0.50	0.39	-1.10	0.75	0.50	0.52	0.70	0.50	0.80	0.09	0.90	0.06
Th	0.10	0.13	0.10	0.84	-0.40	0.96	-0.30	0.98	-	-	-	
Se	-0.10	0.09	-1.20	0.98	0.10	0.07	0.40	0.71	0.10	0.00	0.40	0.52
In	-1.20	0.77	-1.20	1.06	-0.20	0.68	-0.30	0.75	-	-		
Be	-3.7	1.80	-1.50	1.22	-	-	0.10	0.94	-	-	-	
Sm	-1.30	0.84	-1.30	0.89	-	-	-	-	0.30	0.57	0.40	0.53
As	0.40	0.26	-	-	-	-	-	-	-	-	-	-
Bi	-	-	-	-	0.30	0.64	0.10	0.78	-	-		
Hg	-				0.40	0.66	0.40	0.79				
Al	-	-	-	-	0.20	0.71	0.20	0.88	0.60	0.36	0.70	0.34
La	-	-	-	-	0.40	0.64	0.30	0.68	0.50	0.39	0.50	0.42

References

[1] *G. Alberti* and *G. Grassini*, J. Chromatogr. 4, 423 (1960).

[2] *G. Grassini* and *C. Podiglione*, ibid, 13, 561 (1964).

[3] *M. A. S. Jeronimo* and *M. J. Nunes Da Costa*, ibid, 5, 546 (1961).

[4] *M. J. Nunes Da Costa* and *M. A. S. Jeronimo*, ibid, 5, 456 (1961).

[5] *J. P. Adolff*, ibid, 5, 365 (1961).

[6] *M. N. Sastri* and *A. P. Rao*, ibid, 9, 250 (1962).

[7] *J. M. P. Cobral*, ibid, 4, 86 (1960).

[8] *H. Schroeder*, ibid, 6, 361 (1961).

[9] *J. Prasilova* and *F. Sebesta*, ibid, 14, 555 (1964).

[10] *Pe Haiyin* and *Yung Hsiang, Chu Hua, Hsuch*, Hsuch Pas 32, 103 (1966).

[11] *M. Qureshi* and *S. Z. Qureshi*, J. Chromatogr. 22, 198 (1966).

[12] *Shih Nien Shen, Zhun Zhang* and *Hneiven Chang*, Acta Chim. Sinica 30, 21 (1964).

[13] *Zhu Jun Zhang, Ying Bo-Hai, Ting Zhen Bang* and *Shih Hien Shen*, ibid, 31, 218 (1965).

[14] *M. Qureshi* and *K. G. Varshney*, J. Inorg. Nucl. Chem. 30, 3081 (1968).

[15] *M. Qureshi, I. Akhtar* and *K. N. Mathur*, Anal. Chem. 39, 1766 (1967).

[16] *M. Qureshi* and *K. N. Mathur*, Anal. Chim. Acta. 41, 560 (1968).

Received: May 17, 1976

Accepted: Aug. 10, 1976

SEPARATION SCIENCE, 12(6), pp. 649-655, 1977

NOTE

2·28

Cation Chromatography on Stannic Tungstate Thin Layers in DMSO–Acid and Aqueous DMSO Systems: Quantitative Separation of Gold from Numerous Metal Ions

M. QURESHI and K. G. VARSHNEY

CHEMISTRY SECTION Z.H. COLLEGE OF ENGINEERING AND TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY, ALIGARH, INDIA

S. P. GUPTA and M. P. GUPTA

CHEMISTRY DEPARTMENT, D.N. COLLEGE
MEERUT (U.P.), INDIA

Abstract

Thin-layer chromatography of metal ions has been performed on stannic tungstate using solvent systems containing dimethyl sulfoxide. Such binary separations as Fe–Al, La–Pr, La–Nd, Cr–Al, Tl–In, Fe–Mn, and Cr–Mn have been achieved. Gold (100 to 240 μg) has been separated quantitatively from vanadium, chromium, cerium, iron, cobalt, nickel, bismuth, manganese, titanium, and thorium in DMSO: water (1:1), and the method has been found to be precise and accurate.

INTRODUCTION

Thin-layer chromatography was first applied to separate inorganic cations by Seiler and co-workers (*1–5*). A review by Brinkman (*6*), however, showed that most of these separations were effected on thin layers of silica gel. Some studies on thin layers of other inorganic ion exchangers have been reported (*7–21*), but in most of them the use of binders such as silica gel, starch, or cellulose makes it difficult to have a clear interpretation of the mechanism. In these laboratories we have been able to prepare binder-

free layers of the inorganic ion exchange materials stannic antimonate (*22*) and stannic arsenate (*23*). These layers have been used successfully for the quantitative separation of UO_2^{2+} from numerous metal ions and for the separation of Hg^{2+} from Cd^{2+} and Zn^{2+}. It is essential to search for thin layers which may be selective for certain metal ions. With this end in view, stannic tungstate thin layers were tried because this material has previously been found to be quite stable in acids and to have good ion exchange properties (*24*). We have used this inorganic ion exchanger in paper (*25*) and electrochromatography (*26*) to achieve various useful separations of inorganic cations. The present work is in continuation of our attempts to prepare thin layers without a binder and to use them for the quantitative separation of metal ions. Dimethyl sulfoxide (DMSO) has been used as a developer because it has earlier shown a great potential for separations (*22*). As a result, many useful separations have been achieved. Gold has been separated quantitatively from numerous metal ions in a solvent system containing DMSO.

EXPERIMENTAL

Apparatus

Thin layers of stannic tungstate were prepared on glass plates (15 × 3 cm) and the plates were developed in glass jars (20 × 5 cm). A Bausch and Lomb spectronic-20 was used for spectrophotometric studies.

Reagents

Analar grade reagents were used.

Preparation of Ion Exchange Material and Thin-Layer Plates

Stannic tungstate beads in the H^+ form were prepared according to the procedure reported earlier (*24*) by mixing 0.2 *M* solutions of stannic chloride and sodium tungstate solutions in a molar ratio of 2:1. They were powdered and slurried with a little demineralized water in a mortar. The slurry was then spread over the glass plates with the help of an applicator to prepare thin layers of 0.1 mm thickness. The plates were dried in air for use.

Test Solutions and Detection Reagents

The test solutions were generally 0.1 *M* in metal chlorides or nitrates. Conventional spot test reagents were used for detection purposes (*27*).

Procedure

For Qualitative Work

One or two drops of the test solutions were placed on plates with glass capillaries. After the spots had dried, development was made in different solvent systems and the solvent was allowed to rise 10 cm in all the cases. R_1 and R_f values were measured as usual after detection.

For Quantitative Work

A stock solution of gold chloride (~10,000 ppm Au) was prepared in 4 *M* HCl by dissolving auric chloride. A standard spectrophotometric method (*28*) using $SnCl_2$ solution as the coloring reagent was set up for the quantitative determination of gold. Known amounts of gold along with other metal ions were spotted with the help of a micropipette, and the development was performed in a DMSO–water (1:1) solvent system. A pilot plate was run simultaneously in order to locate the exact position of the spot on the working plate. The area where gold was located was scratched, and the mass was eluted with distilled water. The exchanger was separated from the solution by filtration and washed with distilled water 4 or 5 times to ensure complete elution of the gold. The filtrate and the washings were collected in a 25-ml measuring flask. A $SnCl_2$ solution (2 ml) was added to develop the color. This was then made up to 25 ml with distilled water, and the gold was determined spectrophotometrically.

RESULTS

The following solvent systems were used in these studies.

(1) HNO_3–DMSO (6:4, 5.5, 4:6, 3:7, 2:8, 1·9)
(2) HCl–DMSO (6·4, 5.5, 4·6, 3·7, 2·8, 1·9)
(3) DMSO–water (1:1)
(4) HNO_3–water (1·1)

Table 1 summarizes the separations achieved on stannic tungstate thin layers, while Tables 2 and 3 show the quantitative results.

TABLE 1

Separations Actually Achieved on a Stannic Tungstate Thin Layer in Different Solvent Systems

Solvent systems	Metal ion separation ($R_T - R_L$)	Time required (hr)
HNO_3:DMSO (6:4)	Cu (0)-Cd (0.36 0.40)	
	Fe (0)-Al (0.30 0.56)	
	La (0)-Pr (0.80–1.0)	
	La (0)-Nd (0.78–1.0)	
	La (0)-Sm (0.76–1.0)	
	Fe (0)-Au (0.90–1.0)	6
HCl:DMSO (6:4)	Mn (0)-Zn (0.16–0.30)	
	Cr (0)-Al (0.30–0.50)	
	Pt (0.30–0.40)-Au (0.62–1.0)	
	Pd (0.30–0.40)-Au (0.65–1.0)	
	Hg (0.25–0.40)-Au (0.63–1.0)	6
HNO_3:water (1:1)	Cr (0.0)-Al (0.85–1.0)	
	Tl (0.0)-In (0.32–0.55)	
	Fe (0–0.35)-Mn (0.70)–1.0)	
	Cr (0.0)-Mn (0.72–1.0)	2

TABLE 2

Quantitative Separation of Gold in Binary Mixtures

Sample no.	Mixture	Amount of gold applied (μg)	Amount of gold recovered (μg)	Percentage error
1	Au-V	100	105	5
2	Au-Cr	100	102	2
3	Au-Ce	100	105	5
4	Au-Fe	100	105	5
5	Au-Co	100	100	0
6	Au-Ni	100	102	2
7	Au-Bi	100	105	5
8	Au-Mn	100	102	2
9	Au-Ti	100	102	2
10	Au-Th	100	105	5

TABLE 3

Quantitative Separation of Gold from Synthetic Mixtures

Sample no.	Gold applied (μg)	Gold recovered (μg)	Percentage error
1	240	245	+2.1
2	240	240	0.0
3	240	225	−6.25
4	240	225	−6.25
5	160	150	−6.25
6	160	155	−3.1
7	160	150	−6.25
8	160	150	−6.25

DISCUSSION

The present study reveals that stannic tungstate thin layers are highly selective for metal ions, a behavior similar to stannic antimonate and stannic arsenate layers. Almost all metals have zero R_F values in solvent systems containing HNO_3: DMSO in different volume ratios. In some cases a little movement of metal ions is observed which diminishes with an increase of DMSO in the system, and finally in the solvent system HNO_3: DMSO (1: 9) all metals remain at the point of application after development. However, Au^{3+} shows a little movement (R_F = 0.08–0.23) with a change of acid in the solvent system. When we use HCl instead of HNO_3, we observe that the metal ions in general show an increased tendency to move. This is possibly due to the formation of negative chloro-complexes of metal ions which may have greater R_F values on a cation exchanger such as stannic tungstate. Gold is singled out to show higher R_F values than other metal ions, although there is some tailing (R_F = 0.62–1.00). However, if we withdraw acid from the solvent system completely and use only the DMSO: water (1:1) system, only gold and platinum show R_F values, the other ions being stopped at the starting point. Platinum shows a double spot (R_F = 0, 0.68–0.75). This may be because most of the transition metals are strongly bonded to six dimethyl sulfoxide molecules, making the exchange reaction difficult due to steric reasons (*29*). The presence of the anionic species of Au and Pt in acidic solutions may be the cause of a greater movement of these metals on stannic tungstate layers. This behavior of stannic tungstate suggests the possibility of a quantitative separation of gold from other metal ions. In practice, gold has been separated from some binary mixtures containing different

amounts of gold, and it has been noticed that the method works well within an error range of 5% (Table 2). To test the validity of the method and its application in a wider field, some synthetic mixtures were prepared by taking Fe, V, Cr, Ti, Ni, Cu, Ce, and Co along with Au and were applied on the thin layer plates. The results obtained in this manner also show great accuracy and precision (Table 3). When the HNO_3: water (1: 1) system was used for the development of plates, a larger number of cations show a R_f value $\approx$ 1; viz., Be, Al, Mn, Co, Ni, Cu, Zn, rare earths, Au, and Hg. We also obtained a number of important separations such as Cr–Al, Tl–In, Fe–Mn, and Cr–Mn. Thus the most useful solvent systems in these studies are HNO_3:DMSO (6:4), HCl:DMSO (6:4), and HNO_3:water (1:1) which give important binary separations of metal ions. Another striking feature of this study is that HNO_3: DMSO (6: 4) is able to differentiate between movements of lanthanides, thus resulting in their separations. For example, La can be separated from Pr, Nd, and Sm by using this solvent system. DMSO systems generally take larger time for development than water systems because they are highly viscous liquids (viscosity = 2.473 cP at 20°C) with a low freezing point (18.2°C).

Acknowledgments

The authors are thankful to Drs. D. K. Agrawal and P. C. Gupta for facilities and encouragement.

REFERENCES

1. H. Seiler and M. Seiler, *Helv. Chim. Acta*, *43*, 1939 (1960)
2. H. Seiler and M. Seiler, *Ibid.*, *44*, 939 (1961).
3. H. Seiler and W. Rothweiller, *Ibid.*, *44*, 941 (1961).
4. H. Seiler, *Ibid.*, *45*, 381 (1962).
5. H. Seiler, *Ibid.*, *46*, 2629 (1968).
6. U. A. T. Brinkman, G. De Vries, and R. Kurode, *J. Chromatogr*, *85*, 187 (1973).
7. B. A. Zabin and C. B. Rolling, *Ibid.*, *14*, 534 (1964).
8. M. Lesigang, *Mikrochim. Acta*, *1964*, 34.
9. M. Lesigang and F. Hecht, *Ibid.*, *1964*, 508.
10. K. Buchtela and M. Lesigang, *Ibid*, *1965*, 67.
11. M. Lesigang and K. Buchtela, *Ibid.*, *1967*, 1027.
12. G. Alberti, G. Giammari, and G. Grassini-Strazza, *J Chromatogr*, *28*, 118 (1967).
13. G. Alberti, M. A. Massucci, and S. Torracca, *Ibid.*, *30*, 579 (1967).
14. K. H. Konig and K. Demcel, *Ibid.*, *39*, 101 (1967).
15. D. P. Kelley, *Ibid.*, *51*, 343 (1970)
16. K. H. Konig and H. Graf, *Ibid*, *67*, 200 (1972).
17. L. Lepri, P. G. Desideri, and R. Mascherini, *Ibid.*, *70*, 212 (1972).

18. L. Lepri and P. G. Desideri, *Ibid.*, *84*, 155 (1973).
19. R. Kuroda, K. O. Gunia, and H. Watanabe, *Ibid.*, *85*, 167 (1973).
20. R. Kuroda and T. Kunde, *Ibid.*, *80*, 214 (1973).
21. S. W. Husain and S. K. Kazmi, *Experientia*, *28*, 988 (1972).
22. M. Qureshi, K. G. Varshney, and R. P. S. Rajput, *Separ. Sci.*, *11*, 533 (1976).
23. M. Qureshi, K. G. Varshney, and N. Fatima, *Ibid.*, *12*, 321 (1977).
24. M. Qureshi and K. G. Varshney, *J. Inorg. Nucl. Chem.*, *30*, 3081 (1968).
25. M. Qureshi, K. G. Varshney, M. P. Gupta, and S. P. Gupta, *Chromatographia*, *10*, 29 (1977).
26. M. Qureshi, K. G. Varshney, S. P. Gupta, and M. P. Gupta, *Ann. Chim.*, In Press.
27. M. Qureshi and S. D. Sharma, *Anal. Chem.*, *45*, 1283, (1973).
28. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience, New York, 1959, p. 503.
29. V. Gutman, *Coordination Chemistry in Non-Aqueous Solutions*, Springer, New York, 1968, p. 155.

Received by editor December 28, 1976

Annali di Chimica, **66**, *1976* 557

2.29

51/ELECTROCHROMATOGRAPHIC BEHAVIOUR AND SEPARATION OF METAL IONS ON TIN(IV) TUNGSTATE PAPERS

MOHSIN QURESHI (*), K. G. VARSHNEY (*),
S. P. GUPTA (**) and M. P. GUPTA (**)

(*) *Chemistry Section, Z. H. College of Engineering & Technology, Aligarh Muslim University,* Aligarh (India)

(**) *Chemistry Department, D. N. College,* Meerut (India)

Summary. — The electrochromatography of metal ions in different background electrolytes on stannic tungstate papers has been investigated. Different factors such as the use of dimethyl sulphoxide, pH, and the charge of the metal ions have been studied for their influence on the electrophoretic mobility of metal ions. Some important binary and ternary separations have also been achieved by this technique and it was found that the papers are selective for Hg and Zn. The utility of stannic tungstate papers compared to stannic antimonate and stannic phosphate papers has been investigated.

Riassunto. — È stata studiata l'elettrocromatografia su carte al tungstato di stagno(IV) di ioni metallici in presenza di diversi elettroliti di fondo. È stato anche esaminato l'effetto di fattori, quali l'uso di dimetil solfossido, il pH e la carica dello ione metallico, sulla mobilità elettroforetica degli ioni metallici. Con questa tecnica è stato possibile realizzare alcune importanti separazioni di miscele binarie e terziarie ed è stato visto che le carte sono selettive per mercurio e zinco. Le carte al tungstato di stagno(IV) sono state confrontate con quelle all'antimoniato e al fosfato di stagno(IV).

Inorganic ion exchange materials have frequently been used in the electrochromatography of metal ions after Alberti and coworkers [1] first separated La, Pr and Sm by this technique on zirconium phosphate papers. Pe-Hai-Yin [2] separated K, Pb and Cs on ammonium molybdophosphate papers using 0.2 to 0.5 *M* NH_4NO_3 and 0.1 *M* HNO_3 as electrolytes. Qureshi and coworkers [3-6] have also used Sn^{IV} pho-

[1] G. Alberti, A. Conte, G. Grassini, M. Lederer, *J. Electroanalyt. Chem.*, **4**, 301 (1962).

[2] Pe-Hai-Yin, *Hua Hsueh Hsueh Pao*, **31**, 260 (1965).

[3] M. Qureshi, A. H. Israili, *Analyt. Chim. Acta*, **41**, 523 (1968).

[4] M. Qureshi, K. G. Varshney, F. Khan, *Separation Sci.*, **6**, 559 (1971).

[5] M. Qureshi, K. G. Varshney, R. P. S. Rajput, *Ann. Chimica*, in press.

[6] M. Qureshi, R. G. Varshney, *J. Electroanalyt. Chem.*, in press.

sphate, Ti^{IV} tungstate and Sn^{IV} antimonate papers for such studies and achieved some good separations Stannic tungstate was prepared and its ion exchange properties were studied (7) in 1968. Later it was noticed that tungstates generally show high chemical stability compared to that of other exchangers Recently, stannic tungstate papers have been used in paper chromatographic studies (8) and some important separations have been effected. To further explore its utility, stannic tungstate has been tried in electrochromatographic studies.

EXPERIMENTAL

Apparatus

Electrochromatography was performed on « Whatman » No 1 papers of size 36 × 2 75 cm with vertical electrophoresis apparatus (« Systronics », India).

Reagents

Analytical grade reagents were used Stannic chloride pentahydrate was a U S A product

Test solutions and detection reagents

Decimolar solutions of chlorides or nitrates of metal ions used in this study were prepared by standard procedures The oxidation states of these metals were taken as given below, unless stated otherwise

Ag^{I}, Tl^{I}, Be^{II}, Al^{III}, Ti^{IV}, VO_2^{I} Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, Cu^{II}, As^{III}, Se^{IV}, Y^{III}, ZrO^{II}, Cd^{II}, In^{III}, Sb^{III}, La^{III}, Ce^{IV}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Dy^{III}, Hg^{II}, Bi^{III}, Th^{IV}, UO_2^{II} and Nb^{V}

Conventional spot test reagents were used for detection purposes

Background electrolytes

The following solutions were used as the background electrolytes HNO_3 (1 *M*, 10^{-1} *M*, 5×10^{-2} *M*, 10^{-2} *M*, 10^{-3} *M*), HCl (10^{-1} *M*, 5×10^{-2} *M*, 10^{-2} *M*), $HClO_4$ (10^{-1} *M* and 5×10^{-2} *M*), 0 1 *M* HNO_3 + 0 1 *M* KNO_3 (1.1), 0 1 *M* HNO_3 + 0 1 *M* aq DMSO (1 1), 0 1 *M* HCl + 0 1 *M* $HClO_4$ (1:1), 0 1 *M* HCl + 0 1 *M* aq DMSO (1·1), 0 1 *M* $HClO_4$ + 0 1 *M* aq DMSO (1.1).

Preparation of ion exchange papers

The paper strips were first impregnated in an aqueous solution (0 2 *M*) of stannic chloride for 3 5 sec and dried for 15 min on a sheet of filter paper to remove excess of reagent These strips then were treated with an aqueous 0 2 *M* solution of sodium tungstate for 15 sec and again allowed to dry on filter paper at room temperature for 15 min After drying they were washed several times with distilled water to remove unreacted material and placed over sheets of filter paper When dried they were used as such

(7) M Qureshi, K G Varshney, *J Inorg Nuclear Chem*, **30**, 3081 (1968)

(8) M Qureshi, K G Varshney, M P Gupta, S P Gupta, *Chromatographia*, in press

PROCEDURE

The electrophoresis apparatus was filled with 250 ml of background electrolyte in both cathodic and anodic compartments. Stannic tungstate paper strips, which formed the stabilisation medium, were placed in position and allowed to become saturated with the electrolyte. A small drop of the test solution was then applied separately on each strip in the middle using thin glass capillaries.

RESULTS

Based on the migration of the metal ions in different electrolyte solutions the mobility was calculated by applying the formula:

$$\text{Mobility} = \frac{\text{Distance moved (cm)} \times \text{Length of the paper strip (cm)}}{\text{Time (sec)} \times \text{Potential difference (V)}}$$

Negative mobility means the ion moves towards the cathode while positive mobility represents the movement towards the anode.

Table 1 summarizes the separations achieved.

TABLE 1. — SEPARATIONS ACTUALLY ACHIEVED ON STANNIC TUNGSTATE PAPERS BY ELECTROCHROMATOGRAPHY

Background electrolyte	Potential applied and time	Separations achieved
1 *M* HNO_3	100 V, 3 h	Sb—Zn, Ti—Mn
0.1 *M* HNO_3 + 0.1 *M* KNO_3	100 V, 3 h	Al—Fe, Co—Fe, Pb—Cu, Bi—Cd, Se—Cd, Sb—Co, Bi—Mn
0.1 *M* HCl	100 V, 8 h	Cu—Bi—Pb, Cu—Fe, Cd—Cu, Cu—Tl—Pb, Zn—Hg_2^{++}, Zn—Cd, Bi—Th, UO_2—Tl, Fe—Al, Fe—Be, Cr—Al, Cu—Cd, Bi—Sb, Cu—Ag. Hg from 32 cations
0.1 *M* HNO_3 + 0.1 *M* DMSO	100 V, 3 h	Mn—Cr, Zn—Cr, Bi—Ti, ZrO—Pr, Nb—Pr, Ti—Sm
0.1 *M* HNO_3	100 V, 8 h	Be—Al, Be—Fe, Zn—Cd, Pr—Sm, Fe—Al—Be, V—Nb. Zn from 32 ions
0.1 *M* HCl + 0.1 *M* DMSO	100 V, 3 h	ZrO—Ce, Ti—Nd, Hg—Bi, Hg—Pb, Ag—Hg, Hg—Zn, Hg—Ni

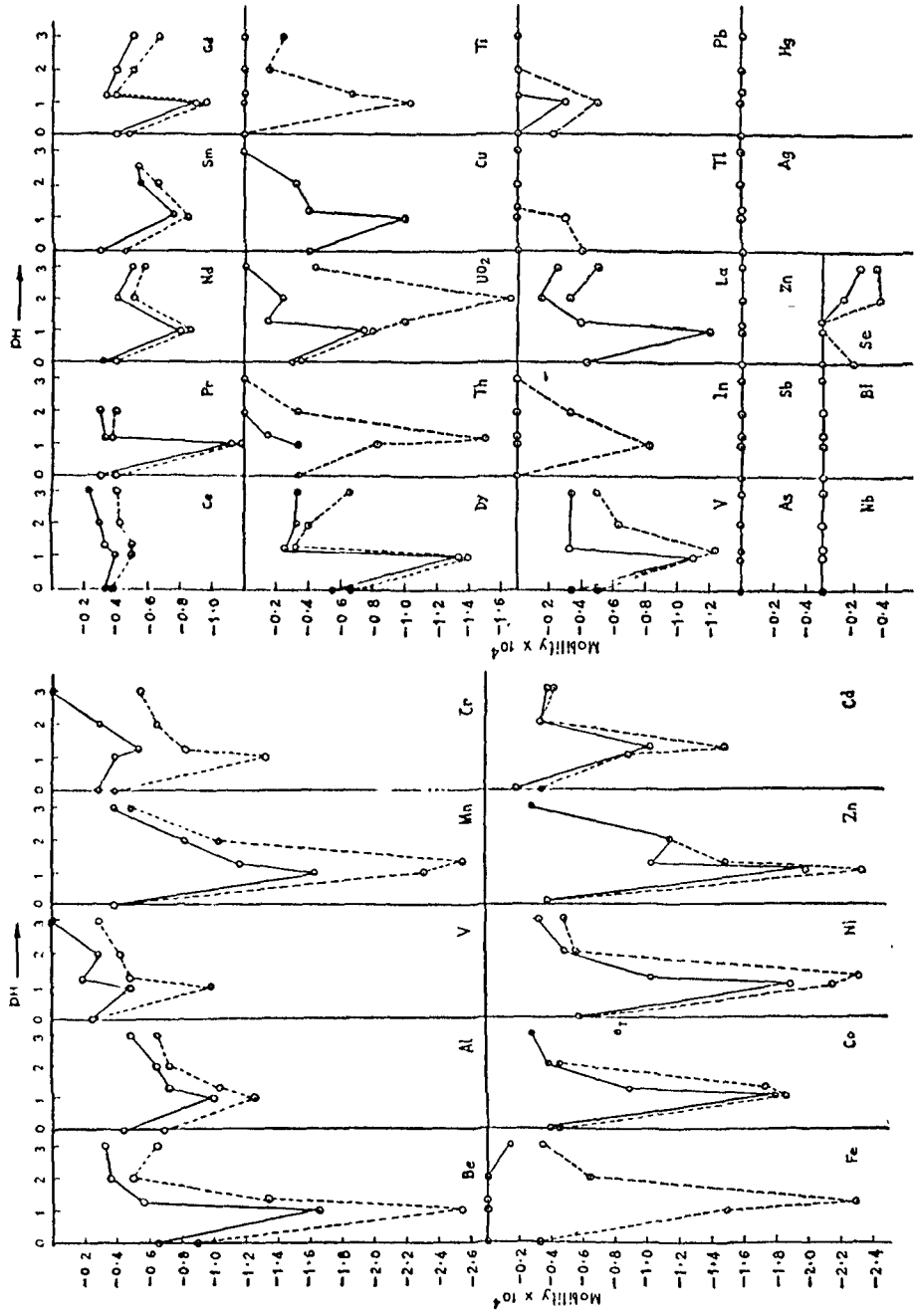


Fig. 1. - Plots of pH *vs* mobility of metal ions. ———: Stannic tungstate papers; — — — —: plain papers.

DISCUSSION

The salient features of this study are the effect of H^+ ion concentration in the electrolyte, charge of metal ions and DMSO on the mobility of metal ions. We shall discuss them individually.

The effect of H^+ ion concentration on the mobility of the metal ions

Figure 1 summarize this effect. It is clear from this figure that all the metal ions have higher mobility on plain papers than on the impregnated papers (because of the ion exchange process or the precipitation of heavy metal tungstates). This is a general behaviour of all the papers impregnated with inorganic ion exchangers. The metal ions have maximum mobility generally at pH $\neq$ 1, probably due to the lower tendency of the metal ions for hydration at this pH. Nb, Bi, Sb and Zr do not move on plain or on impregnated papers at pH = 0-3, as they are easily hydrolysed. Silver and mercury also do not move as they reduced to the metallic form by the cellulose of the paper. Fe, Se, In, Tl, Pb and Ti move on plain papers but do not move on impregnated papers, as they form insoluble tungstates. Selenium has the least mobility at pH = 1 while it shows maximum movement at pH = 3. Similarly, thallium moves to a great extent at pH = 0 on plain papers although it does not move on impregnated papers.

The effect of the charge of the metal ions on the mobility

A plot of the average mobility *vs* charge of the metal ions in some electrolytes (figure 2) shows that, irrespective of the nature of the electrolyte solution, the mobility is a minimum for the tetravalent metals. The average mobility first decreases from monovalent to tetravalent metals due to an increase in the atomic size of the

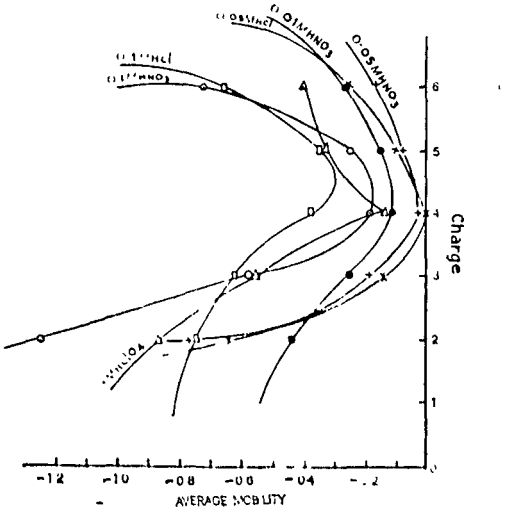


Fig. 2. - Plots of charge on the metal ions *vs* average mobility.

metal. It further increases for the metals having an oxidation number greater than +4. This may be due to the fact that the metals in high oxidation states generally exist as the hydrolysed species, thus bearing a lower charge. For example, in aqueous solution V^{V} and U^{VI} exist as VO_2^+ and UO_2^{+2}, respectively.

THE EFFECT OF DMSO ON THE MOBILITY

Dimethyl sulphoxide has a tendency to increase the mobility of the following cations: Y, La, Pr, Nd, Gd, Dy, Sm, Th and UO_2. This may be due to the solvation effect of DMSO on these metal ions. A lowering effect on the mobility was observed for Ni, Zn, Cd and Co. These metals are known to form complexes [9] with DMSO. Certain metals, such as Sc, ZrO, Nb, Ag, Sb, Bi, and Ti remain unaffected by the presence of DMSO. These are the same metal ions that do not move due to hydrolysis, reduction by paper or the formation of insoluble salts.

However, there are some metal ions which show different behaviour in the presence of different acids such as HNO_3, HCl, and $HClO_4$. The mobility is either increased, decreased or remains unchanged, as indicated in table 2.

TABLE 2. — EFFECT OF DMSO (IN THE PRESENCE OF DIFFERENT ACIDS) ON THE MOBILITY OF SOME METAL IONS

Metal ions	Acids (*)		
	HNO_3	HCl	$HClO_4$
Be	i	d	d
Al	u	d	d
Cr	i	i	d
Mn	u	u	d
Fe	i	i	d
Cu	i	i	d
As	u	i	i
In	i	i	d
Ce	i	i	d
Hg	d	i	u
Ti	i	u	d
Pb	i	i	d
VO_2	d	i	i

(*) i = increase, d = decrease, u = unchanged.

(9) T. C. Waddington, Ed., « Non-Aqueous Solvent Systems », Academic Press, London, 1965, pp. 230-233.

Comparison of mobilities on stannic tungstate, stannic phosphate and stannic antimonate papers

A comparison of the mobilities of metal ions on stannic tungstate, stannic phosphate ([3]), and stannic antimonate ([5]) papers reveals that the metal ions move most on stannic tungstate papers. This is probably due to a smaller ion exchange capacity of stannic tungstate than of stannic phosphate or stannic antimonate. Stannic tungstate papers can, therefore, be used in electrochromatography more advantageously than other, similar, ion exchange papers although it has a lower ion exchange capacity. Thus, certain metal ions which are precipitated on stannic tungstate papers can be separated from other metal ions more easily than on either stannic phosphate or stannic antimonate papers using this technique. This study also reveals that, as in the case with two other papers, almost all the metal ions move towards the cathode, which means that almost all the metal ions remain as positively charged species in the electrolyte solution. The metal ions which do not move at all are again those which form precipitates with stannic tungstate.

Separations achieved

Stannic tungstate papers are selective for Hg and Zn. In 0.1 *M* HCl, Hg, Tl and Bi move towards the anode. However, Hg moves faster and, therefore, can be extracted from all other metal ions on these papers keeping the potential as 100 V and the time of electrophoresis as 8 h. Similarly, Zn can be separated from the rest of the metals in the same electrolyte and under the same conditions because its mo-

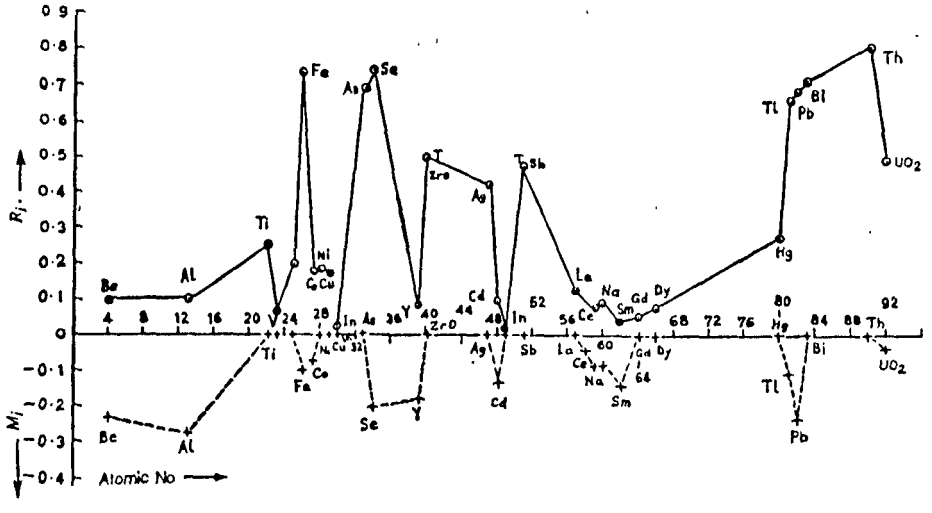


Fig. 3. - Plots of R_f and M_f *vs* atomic number of metal ions in 1 *M* HNO_3 on stannic tungstate papers.

studies have shown that on the introduction of an electric field the papers impregnated with stannic tungstate become more selective for Hg and Zn, the movements of other cations being appreciably enhanced.

We thank Dr. K. D. Agarwal and Dr. P. C. Gupta for research facilities and encouragement.

Received August 12th, 1976.

2.30 A COMPLEXO-ION EXCHANGE METHOD FOR THE SELECTIVE DETERMINATION OF CADMIUM IN SOME ROCKS USING ANTIMONY(V) PHOSPHATE BEADS

KEY WORDS: Cadmium; complexometry; ion-exchange; antimony(V) phosphate; cation exchanger.

Krishna Gopal Varshney*, Sanjiv Mohan Maheshwari and Upma Gupta

Department of Applied Chemistry,
Faculty of Engineering and Technology,
Aligarh Muslim University,
Aligarh-202002 (India).

ABSTRACT

A complexometric method has been proposed for the selective determination of cadmium, using antimony(V) phosphate cation exchanger as a masking agent. On the basis of its high selectivity for cadmium antimony(V) phosphate has also been used for several binary, ternary and multinary separations from cadmium. The method has been successfully used for the determination of trace amounts of cadmium in some rock samples such as GSP-1, AGV-1, G-4 and C-6. The method has been found to be precise and accurate and is an

---

*To whom correspondence should be addressed

improvement over the existing direct EDTA titration for cadmium.

INTRODUCTION

Inorganic ion exchangers are well known for their excellent selectivity towards certain metal ions. They have shown ability to separate and concentrate metal ions present in minute amounts. Some of the novel inorganic ion exchangers have shown affinity for heavy metal ions such as Pb, Hg, Cd, Bi etc.[1-4], which are also main source of water pollution. Consequently, separation and determination of these metal ions have been performed by column chromatography using these materials as sorbents. Thus there is a great promise of inorganic ion exchangers in the field of pollution control.

Antimony based inorganic ion exchangers have received attention mainly because of their excellent ion exchange behaviour and stability[5-8]. In our efforts to find an inorganic ion exchanger, suitable for the removal of pollutants from water, antimony(V) phosphate[9] has shown high selectivity for cadmium and mercury. Industrial effluents from electroplating and iron galvanizing plants pollute sources of water with cadmium. Minute amounts of cadmium can give rise to

nephrotoxic and cardiovascular changes. It tends to accumulate in liver, kidneys and thyroid glands of human beings.

Disodium salt of ethylene diamine tetra-acetic acid is a well known complexing agent[10] for the majority of metal ions at varying pH. The complex formation of EDTA with cadmium and mercury occurs at pH $\sim$ 4. However, many other metals interfere in this determination because the EDTA-metal complexes are readily formed and are stable.

The present method is an effort to modify the method for a more selective determination of cadmium in trace amounts. Antimony(V) phosphate has been utilized as a masking agent.

EXPERIMENTAL

Reagents and chemicals

Antimony(V) chloride used was of $\sim$ 9 8% purity obtained from Fluka, Switzerland and the trisodium orthophosphate was a B.D.H. Poole (England) product.

Cadmium nitrate solution, 0.1M

EDTA solution, 0.05M

Copper nitrate solution, 0.01M

PAN indicator, 0.1% in methanol

Solutions of various cations were prepared of different concentrations. All chemicals and reagents were of

AnalaR grade.

Buffers

The buffer solutions of different pH values were obtained by mixing the 0.2M aqueous solutions of sodium acetate and acetic acid in varying ratios as shown below:

Mixing ratios of acetic acid and sodium acetate	pH of the buffer
10:0	3.1
9.5:0.5	3.45
8.0:2.0	3.85
6.0:4.0	4.30
3.0:7.0	4.85
0.5:9.5	5.75
0:10	8.75

Rock samples

Both standard[11] (AGV-1 and GSP-1) and raw rocks (G-4 and C-6) were used in these studies. They are known to contain the following elements in major and trace amounts:

Major amount - Si, Al, Fe, Ti, Mg, Ca, Na, K, P, Mn.

Trace amount - Ni, Cr, Co, Rb, Sr, V, Ba, Cd, Zn, Pb, Cu, Zr, Y, Ga, Nb.

Synthesis of the ion exchange material

Antimony(V) phosphate (SbP) was synthesized[9] as follows:

Antimony(V) chloride (0.1M) and trisodium orthophosphate (0.05M) solutions were mixed in a volume ratio 1:1 adjusting the pH of the solution at 0-1. The gel thus obtained was kept for 24 hours at room temperature ($\sim 30^{\circ}C$) and filtered by suction. The excess acid was removed by washing with demineralized water (DMW) and the material was dried in an air oven at $45^{\circ}C$. The dried gel which cracked into small granules when put in DMW was converted into the H^+-form by treating with approximately 1M HNO_3 for 24 hours with occasional shaking and intermittently replacing the supernatant liquid. The material thus obtained was finally washed to a pH 6-7 and dried as above before sieving to a uniform size (60-100 mesh). The Na^+-ion exchange capacity obtained by column process was found to be 1.75 meq/dry g.

Equilibrium studies

In order to ascertain the equilibrium time for the exchange process on antimony(V) phosphate beads, various solutions (5 ml) containing known amounts of cadmium (505 µg) at pH-4 with an excess of EDTA (0.05M)

solution. This solution was then shaken with 500 mg of the ion exchanger in Na^+-form for different time intervals. Figure-1 shows the amount of Cd^{2+} released with time. It indicates that 7 hours are required for the equilibrium to establish. The exchanger in H^+-form however did not give a satisfactory result as precipitation occurs in the solution on standing.

Determination of cadmium

(a) In synthetic mixtures

Some binary, ternary and multicomponent mixtures were prepared by adding different metal ions alongwith Cd^{2+} (2.69 to 809 μg).

To the 10 ml of this solution were added an excess of the EDTA (0.05M) solution and 20 ml of the buffer solution of pH 4. This mixture was then heated for a few minutes before cooling to the room temperature and diluting upto 100 ml with DMW.

5 ml of this solution was back titrated using copper nitrate solution as a titrant and PAN as an indicator, maintaining the pH at 4 to determine the amount of EDTA left unreacted.

Another 5 ml portion of the above solution was shaken with 500 mg of SbP for 7 hours. The EDTA liberated was titrated with copper nitrate as described

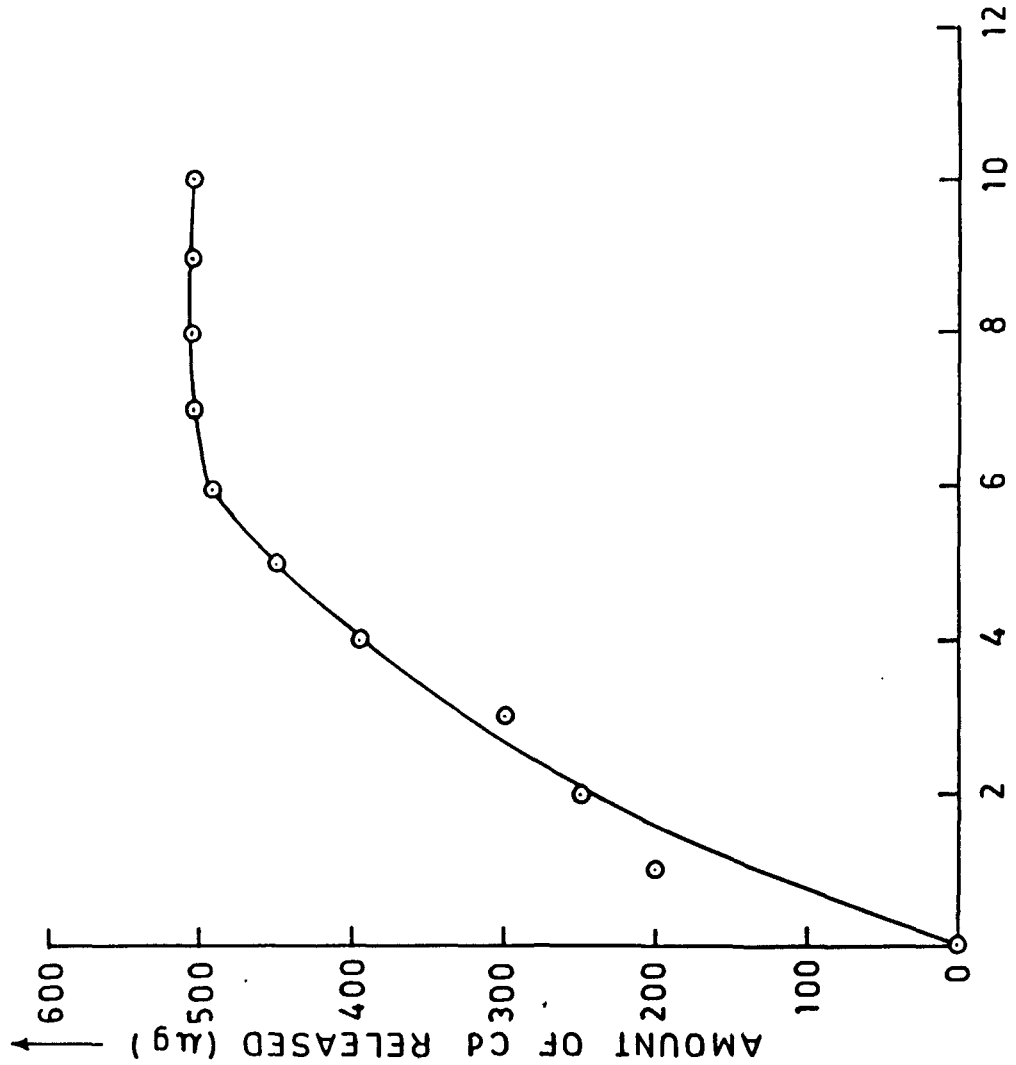


FIG.1- EFFECT OF TIME ON THE RELEASE OF CADMIUM FROM THE Cd - EDTA COMPLEX BY THE ADDITION OF SbP AT pH-4

above and the results are given in Table-1.

(b) In rock samples

1 gm of the rock sample was taken in a nickel crucible containing 20 ml of a 20% NaOH solution. The crucible was put in a muffle furnace at 900°C for about an hour. The residue was cooled to the room temperature and leached with 4M HCl. It was further diluted to 100 ml with ~ 2M HCl to obtain the stock solution.

Fusion of 1 gm of the rock sample with solid NaOH in a nickel crucible also resulted the same solution.

10 ml of this solution was evaporated to dryness to remove excess of acid and the residue was taken up in a fixed volume of the EDTA (0.05M) solution. 4 ml of the buffer solution (pH 4) was added to maintain the pH. This solution was then shaken with 500 mg of SbP and the liberated EDTA was back titrated as above. The results are shown in Table-2.

Effect of pH on the determination of cadmium

In a several conical flasks were taken 809 µg of cadmium and the procedure as reported above was followed for its determination at various pH maintained with the help of the buffer solutions. The amounts found were plotted against pH to obtain the results as

TABLE 1

Determination of Cadmium in Presence of Other Metal Ions by the Proposed Method.

Sl. No.	Interfering Ion (μg)		Cadmium (μg)		% Error	RSD* (%)
			Taken	Found		
1.	Mn(II)	239	505	500	-0.99	0.20
		23.9	25.2	24.9	-1.19	
		119	505	501	-0.79	
2.	Co(II)	294	505	497	-1.47	1.77
		29.4	25.2	25.7	+1.98	
		147	505	507	+0.39	
3.	Cu(II)	286	505	510	+0.99	1.30
		28.6	25.2	25.5	+1.19	
		143	505	499	-1.18	
4.	Ni(II)	283	505	508	+0.59	1.55
		28.3	25.2	24.8	-1.58	
		141	505	512	+1.38	
5.	Fe(III)	279	505	510	+1.99	1.08
		27.9	25.2	25.2	0.00	
		139	505	506	+0.19	
6.	Al(III)	78	505	490	-2.97	3.4
		7.8	25.2	26.0	+3.17	
		39	505	493	-2.37	
7.	Hg(II)	600	505	503	-0.39	2.35
		30.0	25.2	26.3	+1.58	
		300	505	512	+1.38	
8.	Mg(II)	121	505	504	-0.19	1.47
		12.1	25.2	24.6	-2.38	
		60	505	507	+0.39	
9.	Ca(II)	220	505	501	-0.79	0.51
		22.0	25.2	24.8	-1.58	
		110	505	502	-0.59	
10.	Ba(II)	306	505	511	+1.18	0.97
		30.6	25.2	25.0	-0.79	
		153	505	506	+0.19	
11.	Sr(II)	549	505	509	+0.79	0.90
		54.9	25.2	25.0	-0.79	
		274	505	509	+0.79	
12.	Zn(II)	245	505	508	+0.59	1.86
		24.5	25.2	24.7	-1.97	
		122	505	490	-2.97	
13.	Pb(II)	1243	505	499	-1.18	2.01
		124.3	25.2	25.9	+2.77	
		621	505	505	0.00	
14.	Bi(III)	941	505	513	+1.58	0.38
		94.1	25.2	25.5	+1.19	
		420	505	509	-0.79	
15.	Fe (9.1) + Cu (9.5)		16.8	17.1	+1.78	
16.	Fe (9.1) + Ni (9.4)		16.8	17.0	+1.19	
17.	Fe (9.1) + Al (2.6)		16.8	16.7	-0.59	
18.	Bi (23.5) + Pb (310)		16.8	16.9	+0.59	
19.	Co (11.76) + Cu (11.44) + Ni (11.32) + Al (3.12) + Hg (24.00) + Pb (49.72) + Fe (11.16) + Mg (4.84) + Ca (8.8).		88.00	90.0	+2.2	

* Relative standard deviation

TABLE 2

Determination of Cadmium in Some Rock Samples by the Proposed Method

Rock sample	Amount of Cd per 5 ml of the rock sample		% Error
	Amount taken (µg)*	Amount found (µg)	
GSP-1	3.20	3.09	-3.43
AGV-1	2.85	2.81	-1.40
G-4	3.65	3.71	+1.64
C-6	4.10	4.21	+2.68

*As verified by atomic absorption spectrophotometer.

shown in Figure-2. This experiment indicates that pH-4 is the optimum pH for the best results.

DISCUSSION

The main feature of this study is to develop a highly selective method for the determination of cadmium. Antimony(V) phosphate is used as a masking agent which breaks the EDTA-Cd complex quantitatively at pH 4. As the results indicate the method is quite precise and accurate and is almost free from any interferences.

Although the material (SbP) is also highly selective for Hg^{2+}, the method does not work satisfactorily

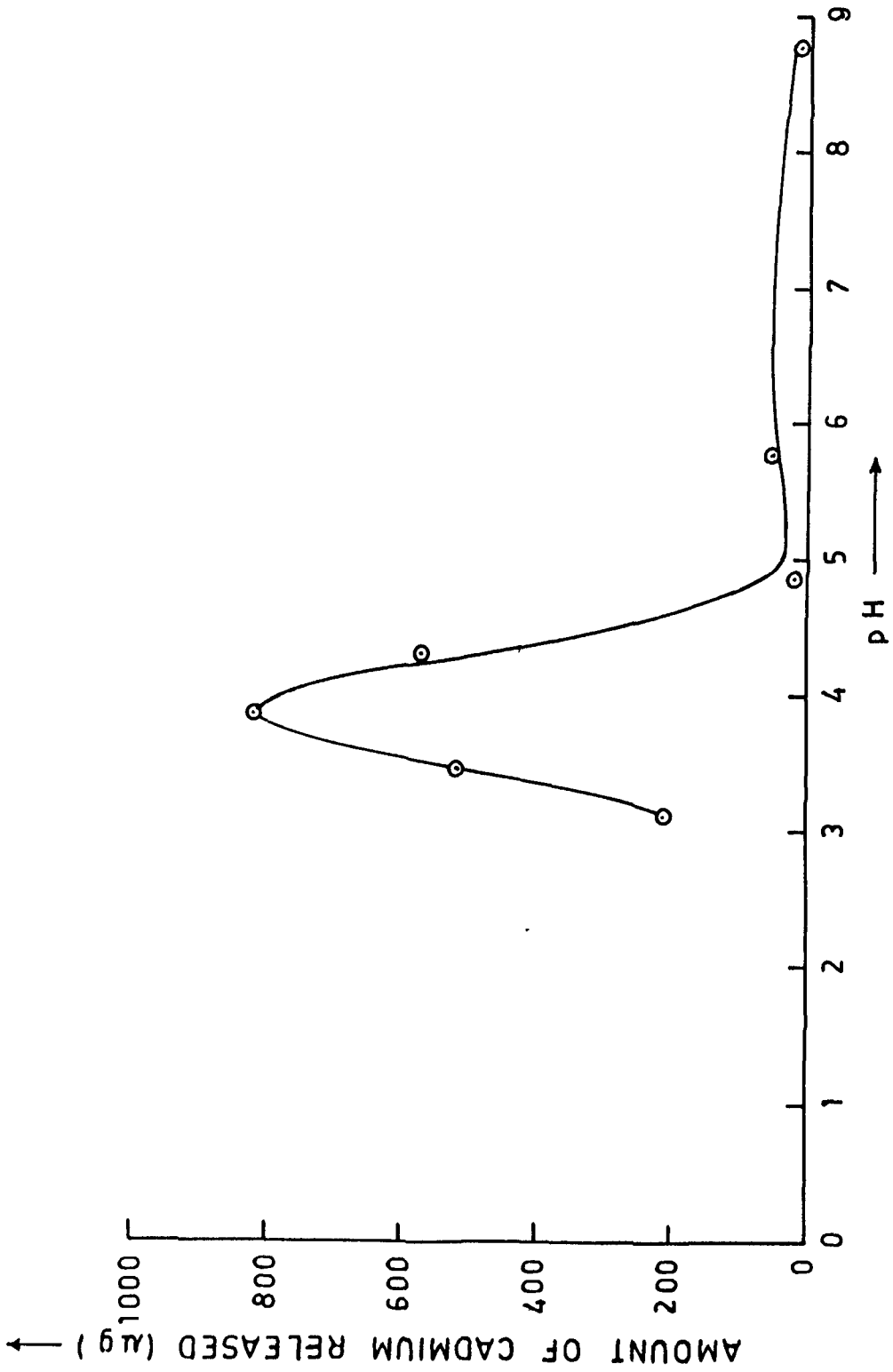


FIG. 2 - EFFECT OF pH ON THE DETERMINATION OF CADMIUM

with this metal ion. The reason may be a difference in the stability constants[12] of the EDTA-metal complexes. Since the EDTA-Cd complex has a lesser stability constant (16.6) at pH-4 as compared to the EDTA-Hg complex (21.9), the latter is not decomposed by the action of antimony(V) phosphate.

The method has been employed for the estimation of cadmium in some rock samples where it is present in traces. The results are in close agreement with those obtained by the atomic absorption spectrophotometer.

ACKNOWLEDGEMENTS

The authors thank Prof. K.T.Nasim for the research facilities and the U.P.Council of Science and Technology, Lucknow for the financial assistance.

REFERENCES

1. J.P.Rawat and K.P.S.Muktawat, Chromatographia, 11, 513 (1978).

2. A.K.De and K.Chaudhury, Talanta, 23, 137 (1976).

3. J.P.Rawat and D.K.Singh, Anal.Chim.Acta, 87, 157 (1976).

4. M.Qureshi, K.G.Varshney and N.Fatima, J.Chromatogr., 169, 365 (1979).

5. M.Abe and T.Ito, Bull.Chem.Soc. (Japan), 41, 333 (1968).

6. L.H.Baetsle and D.Huys, Belg.Patent, 649, 746 (1969).

7. F.A.Belinskaya, E.A.Militsina and T.N.Runeva, Izu. Abad.NauK SSSR, Neorg.Mater, 12, 1631 (1976).

8. B.G.Novikov, F.A.Belinskaya and E.A.Materova, Fhiz.Khim., 1, 94 (1976).

9. K.G.Varshney and S.M.Maheshwari, Ecotox.Environ. Safety, 18, 1 (1989).

10. A.I.Vogel, Text book of Quantitative Inorganic Analysis, 4th revised ed., Clay (The Chaucer Press), Bungay, p. 261 (1978).

11. P.J.Potts, A Handbook of Silicate Rock Analysis, Blackie and Son Ltd. p. 30 (1987).

12. Ref. 10, p. 264.

CHAPTER - 3

KINETICS OF EXCHANGE ON SOME SYNTHETIC INORGANIC ION EXCHANGERS

Colloids and Surfaces, 25 (1987) 131–137
Elsevier Science Publishers B V , Amsterdam — Printed in The Netherlands

3.1

Forward and Reverse Ion-Exchange Kinetics for Na^+–H^+ and K^+–H^+ Exchanges on Crystalline Antimony(V) Silicate

K G VARSHNEY, A A KHAN and S. RANI

Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202001 (India)

(Received 10 September 1986, accepted in final form 8 December 1986)

ABSTRACT

The Nernst Planck equations are applied to study the ion exchange kinetics on the surface of antimony(V) silicate for the Na^+–H^+ and K^+–H^+ exchanges in the forward and reverse directions under conditions favouring particle diffusion. On the basis of these studies, various physical parameters such as the diffusion coefficients, activation energies and entropies of activation are evaluated

INTRODUCTION

Antimony(V) silicate has been synthesized in these laboratories [1], showing excellent chemical stability and ion-exchange behaviour. Its utility has also been explored [1–3] in various fields including the detection of Fe(II) and Mo(VI) and the adsorption of pesticides. The kinetics of the surface phenomena occurring on these materials is also of great importance in understanding the mechanism of the ion-exchange process. Although a large number of kinetic studies on such materials have been reported [4–7], earlier approaches are based on the 'Bt' criterion [8] which is applicable only for an isotopic exchange process [9,10]. In a true ion-exchange process where the fluxes of two different ionic species are coupled with one another [11], a single diffusion coefficient cannot describe the actual process. A new approach, based on the Nernst Planck equations [12,13] which take into account the exchange of ions having different mobilities to determine the various physical parameters, is therefore applied. The present article also deals with the reversible behaviour of antimony(V) silicate for metal–hydrogen exchanges on its surface.

0166 6622/87/$03.50

EXPERIMENTAL

Reagents and apparatus

Antimony(V) chloride and sodium silicate were products of Koch Light Laboratories Ltd (Colnbrook, Buckinghamshire, U.K.) and Riedel Dettaem A.G. (Seelze Hannover, F.R.G.), respectively. Other reagents and chemicals were of analar grade. For the equilibrium studies a waterbath incubator shaker with a temperature variation of ± 0.5°C was used. A flame photometer by Systronic, India, was used for the quantitative determination of Na^+ and K^+.

Synthesis of antimony(V) silicate

It was synthesized as reported earlier [1]. Its ion-exchange capacities were found to be 1.6 and 1.49 meq/dry g for Na^+ and K^+, respectively.

Kinetic measurements

The material was finely ground and sieved in order to give particles of different mesh sizes (25–50, 52–72, 72–100 and 100–150). Particles of mean radius 121 μm (52–72 mesh) were used in the present study unless stated otherwise. Fractions (20 ml) of 0.005 *N* NaCl or KCl solutions were shaken with the exchanger particles (0.2 g) at various temperatures (20, 35, 50 and 65°C) for different time intervals and the supernatent liquid was analyzed for the metal ions by flame photometry. For the reverse ion exchange the material was taken in the metal form and shaken with 0.01 *N* HNO_3.

RESULTS AND DISCUSSION

These studies illustrate that the ion-exchange process on antimony(V) silicate is controlled by the particle diffusion at and above 0.005 *N* for the metal ion concentration and 0.01 *N* for the H^+ concentration. The difference in concentration between the salt and acid is, perhaps, due to the difference in their ionization. Below these concentrations the film diffusion is more prominent. Under conditions of particle diffusion-controlled exchange, i.e. a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium is given by the equation:

$$U^t(\tau) = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}} \qquad (1)$$

A plot of $U^t(\tau)$ versus t (Fig. 1) indicates that the fractional attainment of equilibrium is faster at a higher temperature, an observation analogous to the

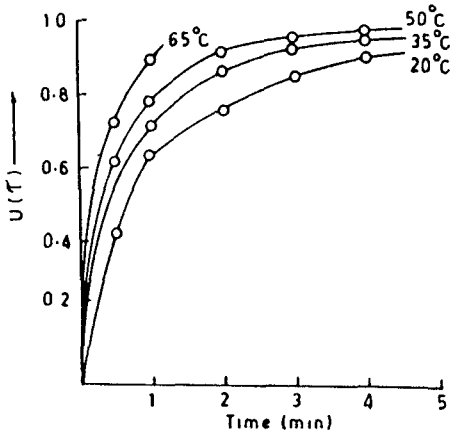


Fig. 1. Plots of fractional attainment of equilibrium against time for the [Na$^+$-H$^+$] exchange on antimony(V) silicate at various temperatures.

earlier one [4–7]. Although this is a limited bath system, the equation applicable to an infinite bath can be used here because $CV \gg \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and exchanger phases, respectively, while V and $\bar{V}$ are the volumes of these phases. Since inorganic ion exchangers do not swell significantly, the Nernst–Planck equations can be solved conveniently with some additional assumptions [11]. As a result we obtained a coupled interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter-ions 'A' and 'B' in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$ the interdiffusion coefficient assumes the value $\bar{D}_A$, 'A' being the counter-ion initially present in the ion-exchanger phase.

The numerical results can be expressed [11] by the explicit approximation:

$$U(\tau) = \{1-\exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{\frac{1}{2}} \quad (2)$$

where $\tau \equiv D_A t/r_0^2$, mobility ratio $\alpha \equiv \bar{D}_A/\bar{D}_M$, r_0 is the particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $0.1 \leqslant \alpha \leqslant 10$ and $Z_H/Z_M = 1$, the charge ratio which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as:

$$f_1(\alpha) = \frac{1}{0.57 + 0.43\alpha^{0.775}}$$

$$f_2(\alpha) = \frac{1}{0.260 + 0.782\alpha}$$

$$f_3(\alpha) = \frac{1}{0.165 + 0.177\alpha}$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained

134

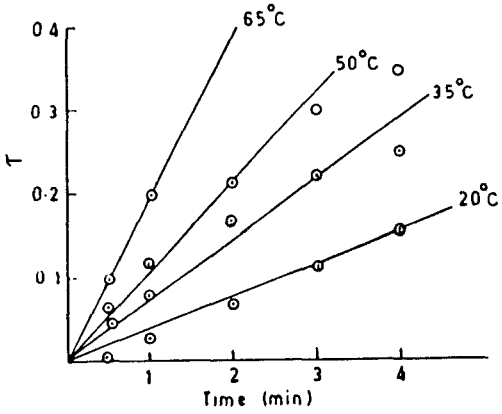


Fig. 2. Plots of τ versus time for the [Na$^+$-H$^+$] exchange on antimony(V) silicate at various temperatures.

by solving Eqn (2) by the graphical method. Plots of τ versus t at the four different temperatures for Na^+-H^+ (Fig. 2) and K^+-H^+, and H^+-Na^+ and H^+-K^+ at a concentration of 0.005 N and 0.01 N, respectively, give straight lines passing through the origin. This confirms that the phenomenon is controlled by particle diffusion. The effect of particle size on the exchange rate is given by Fig. 3 which indicates the reciprocal proportionality between the rate of exchange and the square of the particle size; this again verifies that the diffusion through exchanger particles governs the rate of exchange. Slopes (S) of such lines for all the four exchanges are given in Table 1 which are related to $\bar{D}_A$ as follows:

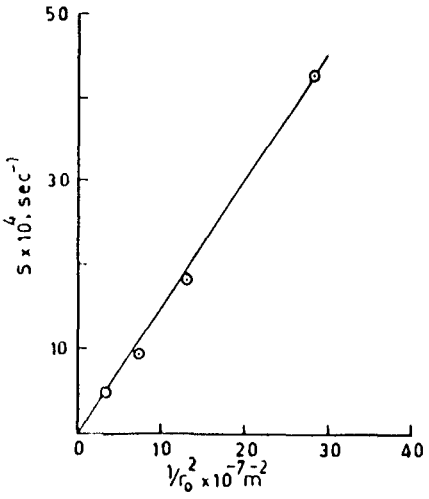


Fig. 3. A plot of slope versus $1/r_0^2$ for the [Na$^+$-H$^+$] exchange at 35°C on antimony(V) silicate.

TABLE 1

Slopes (S) of t plots for forward and reverse exchanges of Na^+-H^+ and K^+-H^+ on antimony(V) silicate

Migration ion	Ion present at ion exchanger	$S \times 10^4$ (s^{-1})			
		20°C	35°C	50°C	65°C
H^+	Na^+	6.11	12.50	18.33	32.50
Na^+	H^+	5.00	9.58	10.83	12.50
H^+	K^+	7.92	9.58	12.08	20.00
K^+	H^+	6.25	8.33	10.67	12.22

$$S = \bar{D}_A / r_0^2 \tag{3}$$

The values of $\log \bar{D}_A$ obtained by this equation are plotted against $1/T$. Straight lines are obtained for Na^+ and K^+ exchanges with H^+ and vice versa for reversible exchange, as shown in Fig. 4, justifying the validity of the Arrhenius equation:

$$\bar{D}_A = D_0 \exp(-E_a/RT) \tag{4}$$

D_0 was then obtained by extrapolating these curves, observing the intercept at the origin and taking the value of $\bar{D}_A$ at 273 K.

The entropy of activation (ΔS^*) is obtained by using Eqn (5)

$$D_0 = 2.72\, d^2 \frac{KT}{h} \exp(\Delta S^*/R) \tag{5}$$

where K and h are the Boltzmann and Planck constants, respectively. d is the

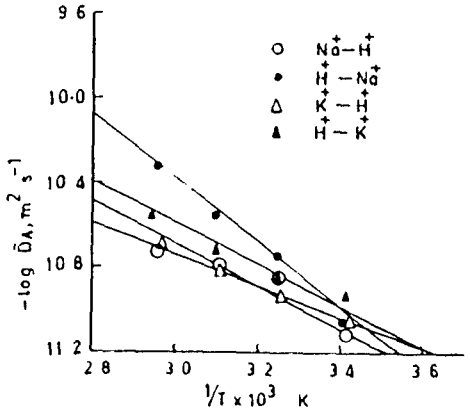


Fig. 4. Plots of $-\log D_A$ versus $1/T$ for the metal-H^+ and H^+-metal exchanges on antimony(V) silicate

136

TABLE 2

Self diffusion coefficient, energies of activation and entropies of activation for forward and reverse exchanges of Na -H and K -H on antimony (V) silicate cation exchanger

Migration ion	Ion present in the exchanger	Hydrated radius of the migration ion (Å)	D_0 (m^2 s^{-1})	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
H	Na	—	8.32×10^{-7}	27.6989	-12.7752
Na	H	2.76	2.88×10^{-8}	19.9585	40.7390
H	K	—	2.19×10^{-8}	18.0302	-43.0161
K	H	2.32	3.98×10^{-9}	14.6324	57.1932

TABLE 3

Half times of exchanges for forward and reverse exchanges of Na -H and K -H on antimony (V) silicate cation exchanger

Migrating ion	Ion present in the exchanger	Half-time exchange, $t_{\frac{1}{2}}$ (s)			
		20 C	35 C	50 C	65 C
H	Na	42	21	18	12
Na	H	66	45	33	25
H	K	45	33	27	21
K	H	45	39	33	28

ionic jump distance taken as 5 Å [14], R is the gas constant and T is taken as 273 K. As the results show, Table 2, D_0, E_a and ΔS^* values decrease with the decrease in hydrated radii of Na^+, K^+ and H^+. A decrease in ΔS^* value also indicates a greater order of exchange. Table 3 shows that the exchange is faster at a higher temperature and that the exchanger is more selective for K^+ ion than for Na^+ ion. This is in accordance with an earlier observation for resins [15].

ACKNOWLEDGEMENTS

The authors are grateful to Professors A.U. Malik and K.T. Nasim for providing research facilities and to the University Grants Commission (India) for financial assistance.

REFERENCES

1 K G Varshney U Sharma S Rani and A Premadas, Sep Sci Tech 17 (1981-1982) 1527
2 K G Varshney, S Rani U Sharma and S Anwar, Anal Lett , 18 (1985) 2033
3 K G Varshney, S Rani and R P Singh, Ecotoxicol Environ Saf , 10 (1985) 309
4 K G Varshney, S Agarwal and K Varshney, Acta Chim Hung , 69 (1984) 116
5 K G Varshney, S Agrawal and K Varshney, Colloids Surfaces, 9 (1984) 189
6 K G Varshney and S Rani, Indian J Chem , 22 (1983) 657
7 K G Varshney and S Rani Reactive Polymers, 3 (1985) 231
8 G E Boyd A W Adamson and L S Myers, J Am Chem Soc , 69 (1947) 2836
9 R G Herman and A Clearfield J Inorg Nucl Chem , 38 (1976) 853
10 A Dyer and J S Gill, J Inorg Nucl Chem , 39 (1977) 665
11 F Helfferich Ion Exchange, McGraw-Hill, New York, 1962, pp 259-270
12 W Z Nernst, Phys Chem , 2 (1888) 613, 4 (1889) 729
13 M Planck, Am Phys Chem , 39 (1890) 161
14 R M Barrer, R F Bartholomow and L V C Rees, J Phys Chem Solids, 12 (1961) 21
15 F A Cotton and G Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1964, p 321

Reactive Polymers 3 (1985) 231–234
Elsevier Science Publishers B V Amsterdam – Printed in The Netherlands

SHORT COMMUNICATION

3 2

ION-EXCHANGE KINETICS OF SOME DIVALENT METAL IONS ON CRYSTALLINE ANTIMONIC ACID AND ANTIMONY(V) SILICATE CATION EXCHANGERS

K G. VARSHNEY and SIMA RANI

Analytical Laboratory, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh 202001 (India)

(Received August 3 1984, accepted in revised form October 9 1984)

Knowledge of kinetics of exchange on inorganic materials is helpful for the evaluation of their separation potential Most of the earlier studies are based on the Bt criterion [1], which is useful only for an isotopic exchange and not for a true ion exchange process [2], for which the Nernst–Planck equations are more appropriate Since antimonic acid [3] and antimony(V) silicate [4] show promising ion exchange behaviour, we have conducted a kinetic study on the exchange of some divalent metal ions on these materials, the results of which are summarized below

EXPERIMENTAL

Reagents and apparatus

Antimony(V) chloride and sodium silicate were the products of Koch Light Laboratories Ltd (Colnbrook Buckinghamshire, England) and Riedel (De Haen A G (Seelze, Hannover) respectively Other reagents and chemicals were of Analar grade For the equilibrium studies a water bath incubator shaker having a temperature variation of ±0 5°C was used

Synthesis of materials and kinetic measurements

Antimonic acid (SbOH) was obtained [3] by the hydrolysis of antimony(V) chloride, and antimony(V) silicate (SbSi) was synthesized using our earlier method [4] They have a Na^+ ion exchange capacity of 1 9 and 1 6 meq/dry g, respectively They were ground and sieved into different mesh size (25–50, 50–70, 70–100 and 100–150) particles

For kinetic measurements, 20 ml fractions of the cation solutions of concentration 2×10^{-2} *N* were shaken with the exchanger particles (0 2 g) at various temperatures (25, 35, 50, or 65°C) for different time intervals, and the supernatant liquid was analyzed quantitatively for metal ions

RESULTS

These studies illustrate that the ion exchange process on SbOH and SbSi is controlled by particle diffusion at and above a metal ion concentration of 2×10^{-2} *N* Below this concentration film diffusion is more prominent The fractional attainment of equi-

0167 6989/85/$03 30

232

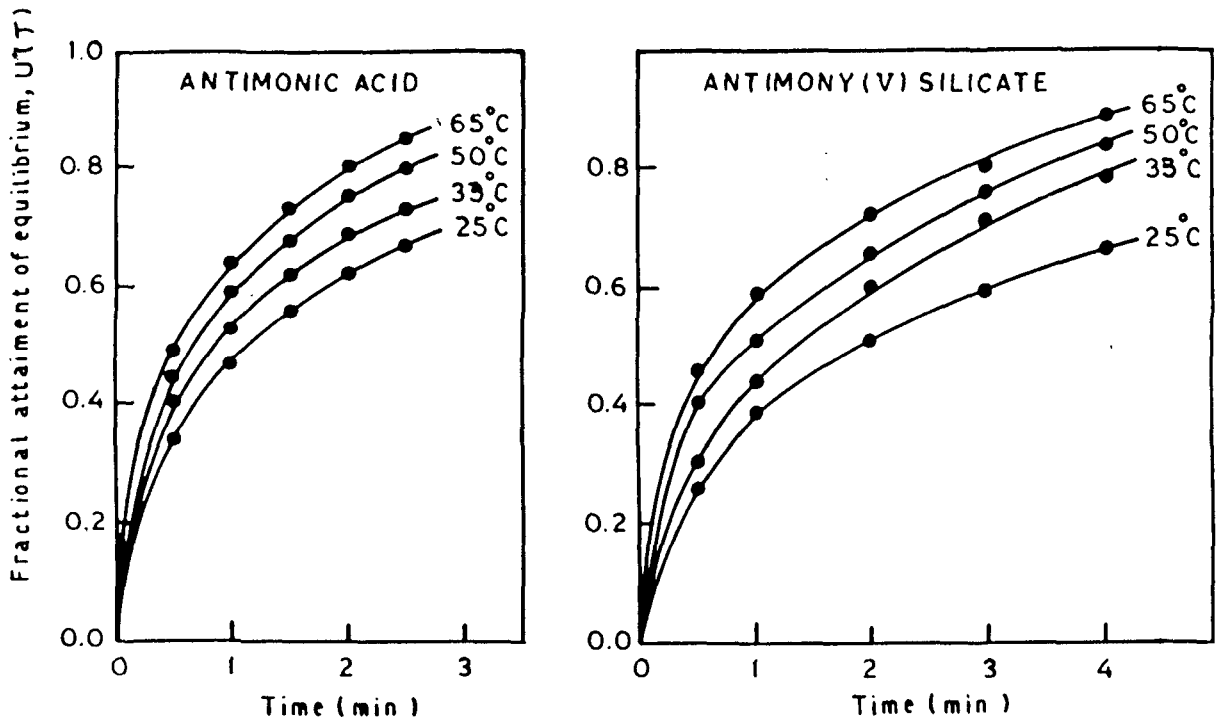


Fig. 1. Plots of fractional attainment of equilibrium versus time for Mn^{2+} on antimonic acid and antimony(V) silicate at different temperatures.

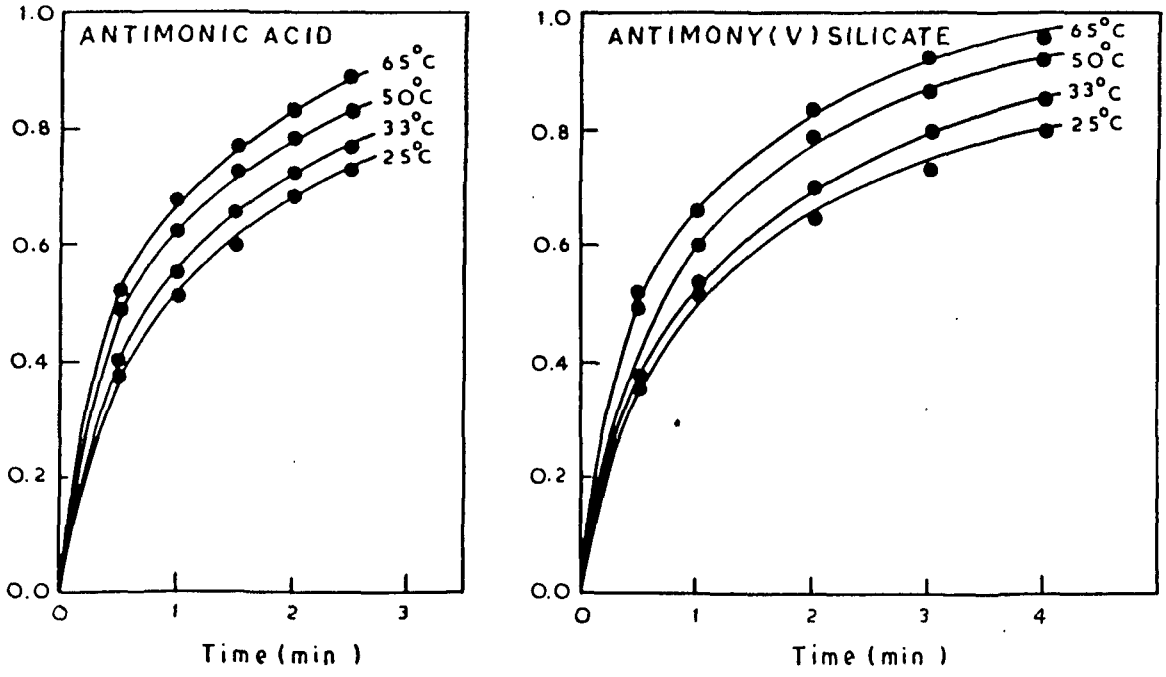


Fig. 2. Plots of fractional attainment of equilibrium versus time for Mg^{2+} on antimonic acid and antimony(V) silicate at different temperatures.

TABLE 1

Slopes S of the various τ versus time plots for transition metals and alkaline earths on antimonic acid and antimony(V) silicate cation exchangers at different temperatures

Metal ion	Particle radius (μm)	$S \times 10^4$ (s^{-1})							
		Antimonic acid				Antimony(V) silicate			
		25°C	33°C	50°C	65°C	25°C	33°C	50°C	65°C
Mn^{2+}	225	–	8 33	–	–	–	6 25	–	–
Mn^{2+}	125	8 33	10 83	13 33	16 67	5 42	7 92	9 79	11 88
Mn^{2+}	78 6	–	12 22	–	–	–	9 17	–	–
Mn^{2+}	62 5		13 89	–	–	–	10 40	–	–
Fe^{2+}	125	7 50	9 58	11 67	14 17	4 79	5 83	7 50	8 13
Co^{2+}	125	9 17	10 83	13 33	16 67	4 79	6 88	10 42	13 13
Ni^{2+}	125	8 33	10 42	13 33	16 25	4 17	5 63	7 08	7 92
Mg^{2+}	225	–	9 44	–	–	–	8 75	–	–
Mg^{2+}	125	10 00	12 78	15 83	20 00	8 33	10 42	14 17	18 33
Mg^{2+}	78 6	–	14 17	–	–	–	12 92	–	–
Mg^{2+}	62 5	–	16 67	–	–	–	14 58	–	–
Ca^{2+}	125	8 89	10 56	12 22	14 17	3 60	4 20	5 00	6 25
Sr^{2+}	125	7 08	7 92	9 17	11 67	5 33	5 00	5 40	6 80
Ba^{2+}	125	8 33	10 00	11 67	13 33	5 20	6 25	8 17	9 40

librium is faster on SbOH than on SbSi, as is clear from Figs 1 and 2 Also, it is faster at a higher temperature, as for the other materials of this class [5 6] Since the inorganic ion exchangers do not swell significantly, the Nernst–Planck equations can be solved conveniently with some additional assumptions [2] The slopes of the τ versus time plots (Table 1) for the metal–H^+ exchange are inversely proportional to the square of the particle radius, r_0, a fundamental condition for particle diffusion The diffusion coefficient, D_0, energy of activation, E_a and entropy of activation, ΔS^*, are summarized in Table 2 for some transition metals and alkaline earths, evaluated by the treatment given elsewhere [7] As these results show, in the case of the transition metals studied, the energy and en-

TABLE 2

Self diffusion coefficient energy of activation and entropy of activation of transition metals and alkaline earths on antimonic acid and antimony(V) silicate cation exchangers

Metal ion exchanging with H^+	Antimonic acid			Antimony(V) silicate		
	D_0 (m^2 s^{-1})	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	D_0 (m^2 s^{-1})	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
Mn^{2+}	$2\,19 \times 10^{-9}$	12 55	−62 16	$1\,45 \times 10^{-9}$	12 34	−65 59
Fe^{2+}	$4\,57 \times 10^{-10}$	11 15	−75 19	$2\,88 \times 10^{-10}$	8 94	−79 03
Co^{2+}	$3\,98 \times 10^{-9}$	14 48	−57 19	$8\,71 \times 10^{-9}$	17 19	−50 68
Ni^{2+}	$1\,95 \times 10^{-9}$	12 33	−63 12	$1\,58 \times 10^{-9}$	13 48	−64 87
Mg^{2+}	$3\,16 \times 10^{-9}$	12 93	−59 11	$7\,59 \times 10^{-9}$	15 63	−51 83
Ca^{2+}	$7\,24 \times 10^{-10}$	9 72	−71 36	$5\,13 \times 10^{-10}$	11 13	−74 23
Sr^{2+}	$9\,33 \times 10^{-10}$	10 98	−69 25	$5\,50 \times 10^{-10}$	11 19	−73 65
Ba^{2+}	$5\,50 \times 10^{-10}$	9 17	−73 65	$8\,32 \times 10^{-10}$	11 24	−70 21

TABLE 3

Half times of exchange for various ions on antimonic acid and antimony(V) silicate at different temperatures

Metal ion	Half time of exchange, $t_{1/2}$ (s)							
	Antimonic acid				Antimony(V) silicate			
	25°C	33°C	50°C	65°C	25°C	33°C	50°C	65°C
Mn^{2+}	69	53	42	30	108	75	57	39
Fe^{2+}	75	60	48	42	123	96	78	66
Co^{2+}	75	60	48	46	156	108	84	72
Ni^{2+}	63	54	42	33	156	96	63	54
Mg^{2+}	57	51	33	27	60	54	42	30
Ca^{2+}	60	48	39	30	138	114	105	75
Sr^{2+}	84	75	60	48	153	105	96	72
Ba^{2+}	64	54	42	36	90	78	60	57

tropy of activation are maximal for the Co^{2+}–H^+ exchange and minimal for the Fe^{2+} H^+ exchange, both on SbOH and SbSi exchangers In case of the alkaline earths these values are maximal for the Mg^{2+}–H^+ exchange However, the two materials differ when we consider the minimum values of these quantities They are minimal for the Ba^{2+}–H^+ exchange on SbOH and for the Ca^{2+} H^+ exchange on SbSi. Table 3 summarizes the half times, $t_{1/2}$, of exchange occurring on the two ion exchangers for the metal ions studied, these half times indicate that the exchange reactions are slow

ACKNOWLEDGEMENT

The Council of Scientific and Industrial Research (India) is thanked for financial assistance

REFERENCES

1 G E Boyd, A W Adamson and L S Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites II Kinetics, J Amer Chem Soc, 69 (1947) 2836

2 F Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, pp 259–270

3 M Abe and I Ito, Synthetic inorganic ion-exchange materials X Preparation and properties of so called antimonic(V) acid, Bull Chem Soc Jpn, 41 (1968) 333

4 K G Varshney, U Sharma, S Rani and A Premadas, Cation-exchange study on a crystalline and thermally stable phase of antimony silicate Effect of irradiation on ion-exchange behaviour and separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II) Ca(II) and Sr(II), Sep Sci Technol, 17 (1982/1983) 1527

5 K G Varshney, S Agrawal and K Varshney, Ion exchange kinetics of alkaline earths on Zr(IV) arsenosilicate cation exchanger Activation energy as a linear function of the ionic mobilities and radii Acta Chim Hung, 116 (1984) 69

6 K G Varshney and U Sharma, Kinetics of exchange of transition metals on zirconium(IV) and thorium(IV) phosphosilicate cation exchangers, Acta Chim Hung 116 (1984) 103

7 K G Varshney, S Agrawal and K Varshney Ion-exchange kinetics of some metal pollutants and their separation on zirconium(IV) phospho- and silico-arsenate cation exchangers, Colloids Surf, 9 (1984) 189

SOLVENT EXTRACTION AND ION EXCHANGE, 2(6), 923-935 (1984)

3·3

A KINETIC APPROACH TO EVALUATE THE ENERGY AND ENTROPY OF ACTIVATION FOR THE EXCHANGE OF ALKALINE EARTH METAL IONS ON TIN(IV) TUNGSTATE CATION EXCHANGER

K.G.Varshney, Asif A.Khan, Kanak Varshney and Sanjay Agrawal

Analytical Laboratories,
Chemistry Section,
Faculty of Engineering & Technology,
Aligarh Muslim University,
Aligarh-202001 (INDIA).

ABSTRACT

A new approach based on the Nernst-Planck equations has been applied to study the reaction kinetics on the surface of tin(IV) tungstate for the Mg(II)-H(I), Ca(II)-H(I), Sr(II)-H(I) and Ba(II)-H(I) exchanges under the conditions favouring a particle diffusion phenomenon. On the basis of these studies the various physical parameters such as the effective diffusion coefficients, activation energies and entropies of activation have been evaluated which give some informations regarding the mechanism of ion-exchange on the surface of inorganic materials.

INTRODUCTION

Inorganic ion exchangers are well established materials for the separation of metal ions (1,2). The rate factor in the ion-exchange process is of great importance for the economic and industrial employment

 0736-6299/84/0206-0923$3.50/0

of ion exchangers. Although a large number of kinetic studies on such materials have been reported (3-9), these earlier approaches are based on the 'Bt Criterion' (10) which is applicable only for an isotopic exchange process (11,12). In a true ion-exchange process where the fluxes of two different ionic species are coupled with one another (13), a single diffusion coefficient can not describe the actual process. This article summarizes our efforts to apply the Nernst-Planck equations (14,15) which take into account the exchange of ions having different mobilities to determine the various physical parameters. Tin(IV) tungstate has been selected because it has shown high chemical stability (16) and some important analytical separations have been carried out with this exchanger (17).

EXPERIMENTAL

Reagents and Chemicals

Stannic chloride pentahydrate and sodium tungstate (B.D.H.Analar) were used. All other chemicals were of reagent grade.

Apparatus

A water-bath incubator shaker having a temperature variation of $\pm$ 0.5 °C was used in the equilibrium studies.

Synthesis, Ion-exchange Capacity and Composition of the Exchanger

Tin(IV) tungstate was synthesized by the method reported (16) earlier as follows: Aqueous solutions of 0.02M stannic chloride and 0.02M sodium tungstate were mixed in the molar ratio 2:1. The gel was digested at room temperature for several hours,

washed with water, filtered and dried at room temperature. On immersion in water it broke down to small particles with cracking and slight evolution of heat. It was converted to the hydrogen form by immersion in dil HNO_3 for 24 hr, the acid being intermittently replaced; it was then washed several times with water until the pH of the washing water was 6. Finally it was filtered and dried in air. The total ion-exchange capacity of the exchanger for Na^+, obtained by the column process, was 0.50 meq/g which is the same as reported earlier (16). The composition was also determined by the standard methods (18-20) which confirmed the earlier results showing the molar ratio of Sn to W as 3:1.

Kinetic Measurements

Tin tungstate was ground well in order to give particles of different mesh sizes (50-70, 70-100, and 100-150). Particles of mean radii 125 μm (50-70 mesh size) were generally used unless stated otherwise. 20 ml fractions of the metal ion solutions (Mg, Ca, Sr and Ba) were shaken with 200 mg of the exchanger (H^+ form) in several stoppered conical flasks at the desired temperatures (20, 30, 45 and 60 °C, ± 0.5 °C) for different time intervals. Supernatant liquid was immediately removed and analyzed for its metal ion content. Each run was repeated six times to evaluate the standard deviation in the results obtained.

RESULTS AND DISCUSSION

A study of the concentration effect on the rate of Mg(II)-H(I) exchange at 30 °C was made using different concentrations (0.005, 0.01, 0.02, 0.03 & 0.05M). It shows that the initial rate of exchange

is proportional to [Mg(II)] upto a concentration $< 0.03M$ and becomes constant at and above this concentration. Under the conditions of particle diffusion control (solution concentration being taken as 0.03M), a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium may be given as

$$U(\tau) = \frac{\text{the amount of exchange at time t}}{\text{the amount of exchange at infinite time}}$$

The amount of exchange at infinite time corresponds to the exchange at equilibrium, which is attained after one hour of shaking as confirmed by the exchange versus time plots. The values in meq/g (Mg,0.50; Ca,0.60; Sr,0.67; Ba,1.2) are comparable with the exchange capacity of the material for the metal ions studied. The standard deviation in the determination of $U(\tau)$ for all the 4 metal ions was $< 18 \times 10^{-3}$ (abs.) for six measurements. Table 1 shows the results for Mg(II). Further calculations for the different parameters were made using the mean value of $U(\tau)$ at a particular time and temperature. Although, the present system is a 'limited bath' the equation applicable to an 'infinite bath' can be used here because $CV \gg \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and the exchanger phases, respectively, while V and $\bar{V}$ are the volumes of these phases. The Nernst-Planck equations can be solved with some additional assumptions (13) which are valid for inorganic ion-exchangers as the swelling changes and the specific interactions are not significant in this case. As a result we obtain a coupled

TABLE 1 STANDARD DEVIATION IN $U(\tau)$ VALUES FOR Mg(II) AT DIFFERENT TEMPERATURES

Time (min)	$U(\tau)$ (mean value of six replicates)				Standard deviation (abs.) x 10^3			
	20°C	30°C	45°C	60°C	20°C	30°C	45°C	60°C
1.0	0.58	0.63	0.65	0.71	9.96	8.16	8.08	6.53
1.5	0.69	0.73	0.76	0.80	8.6	8.97	9.27	7.15
2.0	0.77	0.81	0.83	0.85	17.67	12.85	7.44	6.60
2.5	0.83	0.84	0.89	0.91	6.98	7.16	7.82	8.21
3.0	0.88	0.89	0.91	0.94	12.11	8.67	7.82	7.15

interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions 'A' and 'B' in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$, the interdiffusion coefficient assumes the value $\bar{D}_A$, 'A' being the counter ion initially present in the ion-exchanger phase. Since in the present study the exchanger is taken in the H^+-form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Making use of the Nernst-Planck equations the numerical results can be expressed by the explicit approximation (13)

$$U(\tau) = \left\{1-\exp\left[\Pi^2 \left(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3\right)\right]\right\}^{\frac{1}{2}} \quad \ldots \quad (1)$$

where $\tau \equiv \dfrac{\bar{D}_H\, t}{r_o^2}$ and the mobility ratio is, $\alpha \equiv \dfrac{\bar{D}_H}{\bar{D}_M}$,

r_o = particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leqslant \alpha \leqslant 20$ and $\dfrac{Z_H}{Z_M} = \dfrac{1}{2}$ which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed (13) as

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}} \qquad (a)$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}} \qquad (b)$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.14}} \qquad (c)$$

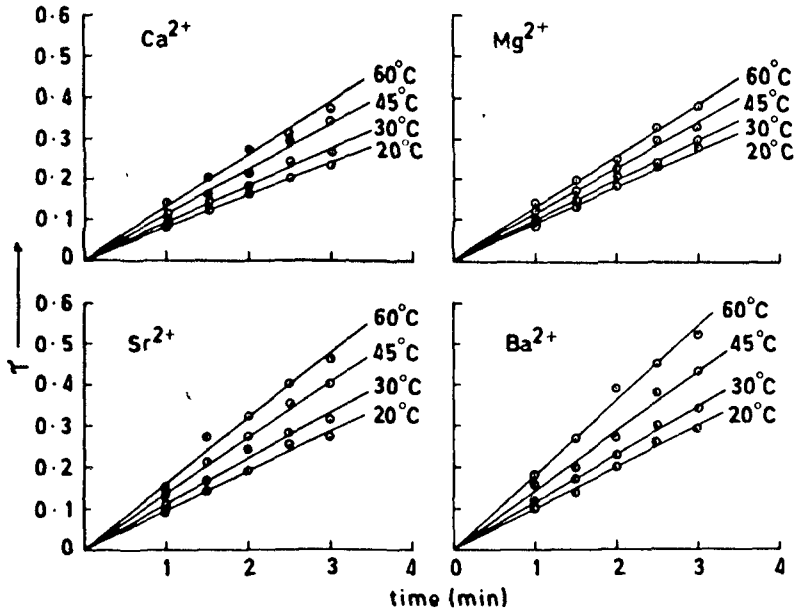


FIGURE 1 Plots of τ vs. t for Ca^{2+}-H^+, Mg^{2+}-H^+, Sr^{2+}-H^+, and Ba^{2+}-H^+ exchanges at different temperatures on tin(IV) tungstate under the conditions of particle diffusion.

Each value of $U(\tau)$ has a corresponding value of τ which is obtained from equation (1). Plots of τ vs. t at different temperatures (Fig.1) for Mg(II) ion are shown at a concentration 0.03M, which are straight lines passing through the origin, confirming a particle diffusion controlled mechanism at this concentration. Slopes (S) of such lines for all the four alkaline earths are given in Table 2.

The particle size seems to have a marked effect on the exchange rate. A plot of S vs. $1/r_o^2$ (Fig.2) shows the reciprocal proportionality between the rate

TABLE 2 SLOPES(S) OF THE VARIOUS τ VERSUS TIME PLOTS FOR ALKALINE EARTHS ON TIN(IV) TUNGSTATE

Migrating ion	S (s^{-1}) X 10^3			
	20 °C	30 °C	45 °C	60 °C
Mg(II)	1.5	1.67	1.92	2.17
Ca(II)	1.33	1.50	1.83	2.17
Sr(II)	1.58	1.83	2.25	2.67
Ba(II)	1.67	1.92	2.40	3.00

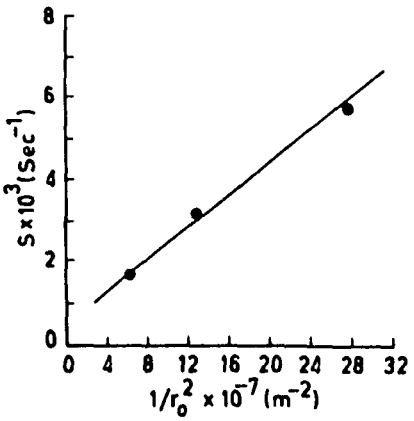


FIGURE 2 Plot of S vs. $1/r_o^2$ for Mg^{2+} at 30 °C on tin(IV) tungstate.

of exchange and square of the particle size which again verifies that the diffusion through exchanger particles is the rate governing step.

The S values are related to $\bar{D}_{II}$ as follows:

$$S = \bar{D}_{II}/r_o^2 \qquad (2)$$

The values of -log $\bar{D}_{II}$ obtained by this equation were plotted against 1/T. Straight lines are obtained for all the metal ions studied, as shown in Figure 3, justifying the validity of the Arrhenius equation:

$$\bar{D}_{II} = D_o \exp(-E_a/RT) \qquad (3)$$

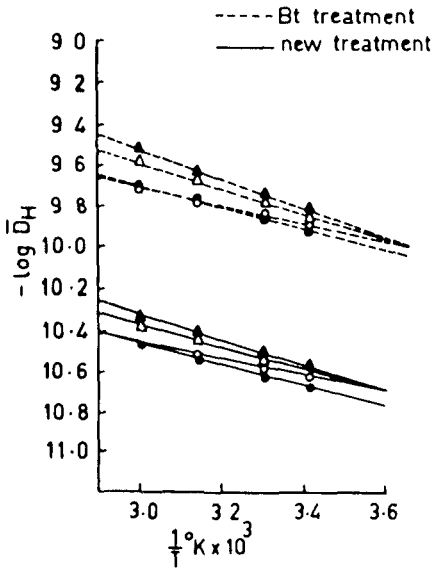


FIGURE 3 Comparative plots of -log $\bar{D}_{II}$ vs. $1/T\,^{\circ}K$ for Mg^{2+} (○), Ca^{2+} (●), Sr^{2+} (Δ), and Ba^{2+} (▲) on tin(IV) tungstate by the new and Bt treatments.

TABLE 3 D_o, E_a AND ΔS^* VALUES OF ALKALINE EARTHS ON TIN(IV) TUNGSTATE IN H^+ FORM

Migrating ion	Ionic mobility ($m^2 v^{-1} s^{-1}$). 10^8	Ionic radius (nm)	Hydrated ionic radius (25) (nm)	D_o ($m^2 s^{-1}$)	E_a (kJ $mole^{-1}$)	ΔS^* (J.deg $mole^{-1}$)
Mg(II)	5.5	0.078	0.310	6.60×10^{-10}	8.150	-72.12
				(5.01×10^{-9})	(8.880)	(-55.27)
Ca(II)	6.2	0.106	0.200	1.26×10^{-9}	10.03	-66.76
				(7.41×10^{-9})	(11.86)	(-52.02)
Sr(II)	6.2	0.127	0.180	1.82×10^{-9}	10.45	-63.70
				(1.95×10^{-8})	(11.92)	(-43.98)
Ba(II)	6.6	0.143	0.150	3.47×10^{-9}	11.92	-58.34
				(4.17×10^{-8})	(13.64)	(-57.66)

The values in parantheses are those derived from the Bt Criterion.

The pre-exponential constants D_o are obtained from the intercepts of the lines while the E_a values can be calculated from the slopes of the plots.

The entropy of activation (ΔS^*) is obtained by substituting D_o into the following equation:

$$D_o = 2.72\, d^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \qquad (4)$$

where k and h are the Boltzmann and Planck constants, d is the ionic jump distance taken (21) as 0.5 nm, R is the gas constant and T is taken as 273 °K. As the results show (Table 3), D_o, E_a and ΔS^* values increase with the ionic mobilities and radii and decrease with the hydrated ionic radii of the alkaline earths, a behaviour analogous to our earlier observations on the other inorganic ion exchangers (22-24). The values obtained of the various physical parameters explain the exchange mechanism of alkaline earths on this ion exchanger. K_d values in DMW oberved earlier (16) on this material are in the order:

$$Ba(II) > Sr(II) > Ca(II) > Mg(II).$$

The same is the order of the mobilities and activation energies as obtained in the present study.

A comparison of the different $\bar{D}_H$ values derived from the present treatment and the Bt Criterion is shown in Figure 3. The $\bar{D}_H$ values obtained by the new treatment give rise to the lower D_o, E_a and ΔS^* values (Table 3) which suggest a more closeness to the physical processes occurring on the ion exchanger beads.

ACKNOWLEDGEMENT

The authors are thankful to Prof. M.Qureshi for research facilities and to the C.S.I.R., India for the financial assistance.

REFERENCES

1. F.C.Nachod and J.Schubert, Ion Exchange Technology, Academic Press Inc., New York, 1956, p. 287.
2. A.Clearfield, G.H.Nancollas, and R.H.Blessing, in Ion Exchange and Solvent Extraction, Vol. 5, J.A.Marinsky and Y.Marcus, Eds., Marcel Dekker, New York, 1973.
3. J.P.Rawat and P.S.Thind, J.Phys.Chem. 80, 1384 (1976).
4. J.P.Rawat and D.K.Singh, J.Inorg.Nucl.Chem. 40, 897 (1978).
5. I.P.Saraswat, R.K.Srivastava, and A.K.Sharma, Can.J.Chem. 57, 1214 (1979).
6. J.P.Rawat and M.A.Khan, J.Inorg.Nucl.Chem. 42, 905 (1980).
7. N.J.Singh, J.Mathew, and S.N.Tandon, J.Phys.Chem. 84, 21 (1980).
8. N.J.Singh and S.N.Tandon, Ind.J.Chem. 19A, 416 (1980).
9. K.G.Varshney and A.Premadas, Ind.J.Chem. 20A, 841 (1981).
10. G.E.Boyd, A.W.Adamson, and L.S.Myers, J.Am.chem. Soc. 69, 2836 (1947).
11. R.G.Herman and A.Clearfield, J.Inorg.Nucl.Chem. 38, 853 (1976).
12. A.Dyer and J.S.Gill, J.Inorg.Nucl.Chem. 39, 665 (1977).

13. F.Helfferich, Ion Exchange, Mc Graw-Hill Book Co., New York, 1962, Ch. 6.
14. W.Z.Nernst, J.Physik.Chem. 2, 613 (1888) and 4, 129 (1889).
15. M.Planck, Ann.Phys.Chem. 39, 161 (1890).
16. M.Qureshi and K.G.Varshney, J.Inorg.Nucl.Chem. 30, 3081 (1968).
17. M.Qureshi, I.Akhtar, and K.N.Mathur, Anal.Chem. 39, 1766 (1967).
18. H.Yagoda and H.A.Falcs, J.Am.chem.Soc. 60, 640 (1938).
19. C.Sterling and W.P.Spuhr, J.ind.Engng Chem. 12, 33 (1940).
20. I.M.Kolthoff and R.Belcher, Volumetric Analysis, Vol. 3, Interscience, New York, 1957, p. 196, 320-22.
21. R.M.Barrer, R.F.Bartholomew, and L.V.C.Rees, J.Phys.Chem.Solids 12, 21 (1961).
22. K.G.Varshney and S.Rani, Ind.J.Chem. 22A, 657 (1983).
23. K.G.Varshney, S.Agrawal, and K.Varshney, Acta Chim. (in press).
24. K.G.Varshney and U.Sharma, Acta Chim. (in press).
25. K.G.Varshney and S.S.Varshney, Chromatographia 10, 542 (1977).

Received by Editor
February 13, 1984

Colloids and Surfaces, 13 (1985) 341—347
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

3.4

ION-EXCHANGE KINETICS OF ALKALINE EARTH METALS ON ZIRCONIUM(IV) ARSENOPHOSPHATE: LINEAR VARIATION OF ENERGY AND ENTROPY OF ACTIVATION WITH IONIC RADII AND MOBILITY

KRISHNA GOPAL VARSHNEY, SANJAY AGRAWAL and KANAK VARSHNEY

Analytical Laboratories, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001 (India)

(Received 23 July 1984; accepted in final form 17 October 1984)

ABSTRACT

The kinetics of Mg(II), Ca(II), Sr(II) and Ba(II) exchange with H(I) on zirconium(IV) arsenophosphate cation exchanger was studied applying the Nernst—Planck equations. The rate of exchange is found to be particle diffusion controlled at a metal-ion concentration $\geq$ 0.01 *M* in aqueous medium. The energy and entropy of activation vary linearly with the ionic radii and mobilities.

INTRODUCTION

Zirconium-based ion exchangers have received attention because of their excellent ion-exchange behaviour and some important chemical applications [1]. Zirconium(IV) phospho- and silico-arsenates prepared earlier in these laboratories have shown a good selectivity for metal ions and reproducibility in ion-exchange behaviour [2, 3]. A kinetic study has also been performed on these materials for the exchange of some transition metals applying the Nernst—Planck equations [4]. Their practical utility has been explored in the detection and separation of metal ions [5, 6] and in the analysis of some real samples, such as rocks and pharmaceuticals, which are rich in alkaline earth metals [7—10]. The following pages summarise the results of our kinetic study to understand the mechanism of exchange of alkaline earth metal ions on zirconium(IV) arsenophosphate cation exchanger.

MATERIALS AND METHODS

Reagents and chemicals

Zirconyl chloride, trisodium orthophosphate and disodium arsenate used in this study were obtained either from BDH (Poole, U.K.) or Merck (Darmstadt, F.R.G.). All other reagents and chemicals were of AnalaR grade.

0166-6622/85/$03.30

Apparatus

A waterbath incubator shaker with a temperature variation of ± 0.5°C was used for the equilibrium studies.

Synthesis of the ion exchanger

Zirconium(IV) arsenophosphate was synthesised by the method described earlier [11]. Its modified phase, obtained by heating at 200°C for 1 h [2], has shown an improvement in its ion-exchange characteristics and chemical stability and was therefore used for the present studies.

Kinetic measurements

The ion exchanger was carefully ground in order to obtain it in different mesh sizes (40–60, 70–100, 100–150, 170–200) and the kinetic measurements were made at 20, 30, 45 and 60°C by the procedure reported earlier [4].

RESULTS AND DISCUSSION

Under the conditions favouring a particle diffusion and at infinite solution volume [12], the fractional attainment of equilibrium, $U(\tau)$, can be expressed by the relation

$$U(\tau) = \{1 - \exp[\pi^2 (f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \quad (1)$$

where τ is $\bar{D}_H t/r_0^2$; mobility ratio, $\alpha = \bar{D}_H/\bar{D}_M$; r_0 is the particle radius; and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leqslant \alpha \leqslant 20$ and the charge ratio, $Z_H/Z_M = 1/2$, which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\,\alpha^{0.668}}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\,\alpha^{0.4635}}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\,\alpha^{1.14}}$$

A solution of Eqn (1) for each value of $U(\tau)$ gives a corresponding value of τ. A study of the τ versus t plots for different metal-ion concentrations (0.005, 0.008, 0.01 and 0.025 *M*) at 30°C indicates that they are straight lines passing through the origin at a concentration $\geqslant$ 0.01 *M* (Fig. 1), suggesting a particle diffusion controlled exchange. It is further confirmed by the

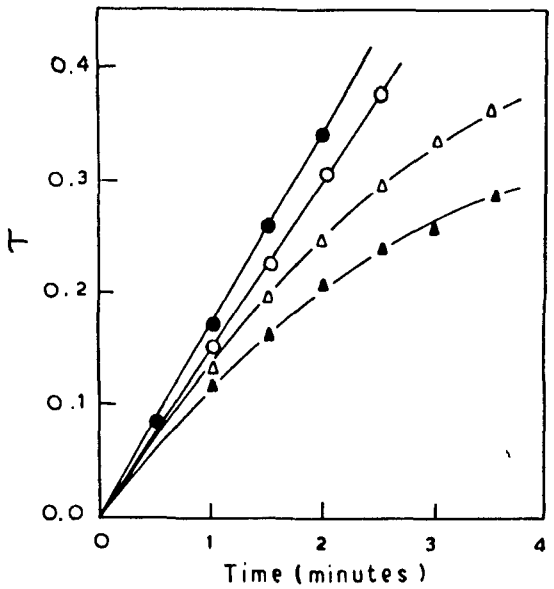


Fig. 1. Plots of τ versus t for Mg(II)—H(I) exchange using different solution concentrations at 30°C: 0.005 M (▲); 0.008 M (△); 0.01 M (○); 0.025 M (●).

TABLE 1

Slopes (S) of τ versus t plots for the alkaline earth metal ions on zirconium(IV) arsenophosphate (r_0 = 150 μm)

Migrating ion	S (s^{-1}) × 10^3			
	20°C	30°C	45°C	60°C
Mg(II)	2.08	2.50	3.33	4.33
Ca(II)	2.08	2.83	4.25	5.25
Sr(II)	2.42	3.33	4.58	6.67
Ba(II)	2.80	3.82	5.42	7.12

inverse variation of the slopes (S) of these straight lines with the square of the particle radii. The S values as summarised in Table 1 are related to $\bar{D}_H$ as follows

$$S = \bar{D}_H / r_0^2 \quad (2)$$

$-\log \bar{D}_H$ values thus obtained vary linearly with $1/T$ (Fig. 2), verifying the Arrhenius equation

$$\bar{D}_H = D_0 \exp(-E_a/RT) \quad (3)$$

The slopes of these straight lines give the energies of activation (E_a), and the intercepts with the Y-axis give the D_0 values, which are related to the entropy of activation (ΔS^*) as

$$D_0 = 2.72\, d^2\, kT/h \exp(\Delta S^*/R) \quad (4)$$

where k and h are the Boltzmann and Planck constants, respectively; d is the ionic jump distance [13] taken as 5 Å; R is the gas constant; and T is taken as 273 K. Table 2 summarises the values of D_0, E_a and ΔS^*. An increase in the values of E_a and ΔS^* with the ionic radii and mobilities [14] of alkaline earth metals is a general behaviour of the inorganic ion exchangers. Figure 3 shows a linear variation of E_a and ΔS^* with ionic radii, hydrated ionic radii and ionic mobilities. Zirconium(IV) arsenosilicate also shows such behaviour [15]. It is in contrast with our earlier observation for transition metals on these materials [4].

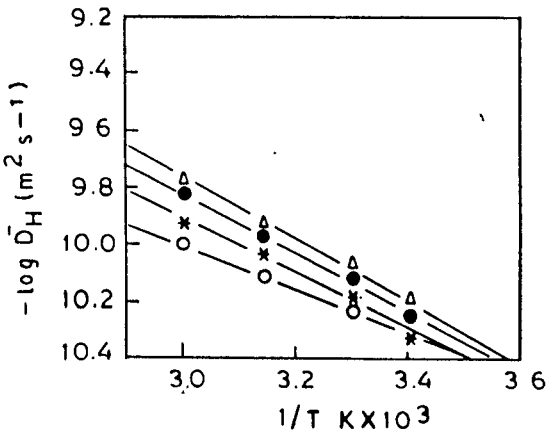


Fig. 2. Plots of $-\log \bar{D}_H$ versus $1/T$ K for Mg(II) (○); Ca(II) (*); Sr(II) (•); and Ba(II) (△).

TABLE 2

D_0, E_a and ΔS^* values for the H^+ exchange with alkaline earth metal ions on zirconium(IV) arsenophosphate

Metal ion exchanging with H^+	Ionic mobility ($cm^2 V^{-1} s^{-1}$)	Ionic radius[a] (Å)	Hydrated ionic radius (Å)	D_0 ($m^2 s^{-1}$)	E_a (kJ mol^{-1})	ΔS^* (J deg^{-1} mol^{-1})
Mg(II)	0.00055	0.78	3.10	2.0×10^{-8}	14.74	−43 79
Ca(II)	0.00062	1.06	2.00	9.5×10^{-8}	18.40	- 30.77
Sr(II)	0.00062	1.27	1.80	1.7×10^{-7}	19.65	- 25 79
Ba(II)	0.00066	1.43	1.50	3.5×10^{-7}	21.11	−20.05

[a]Goldschmidt's value.

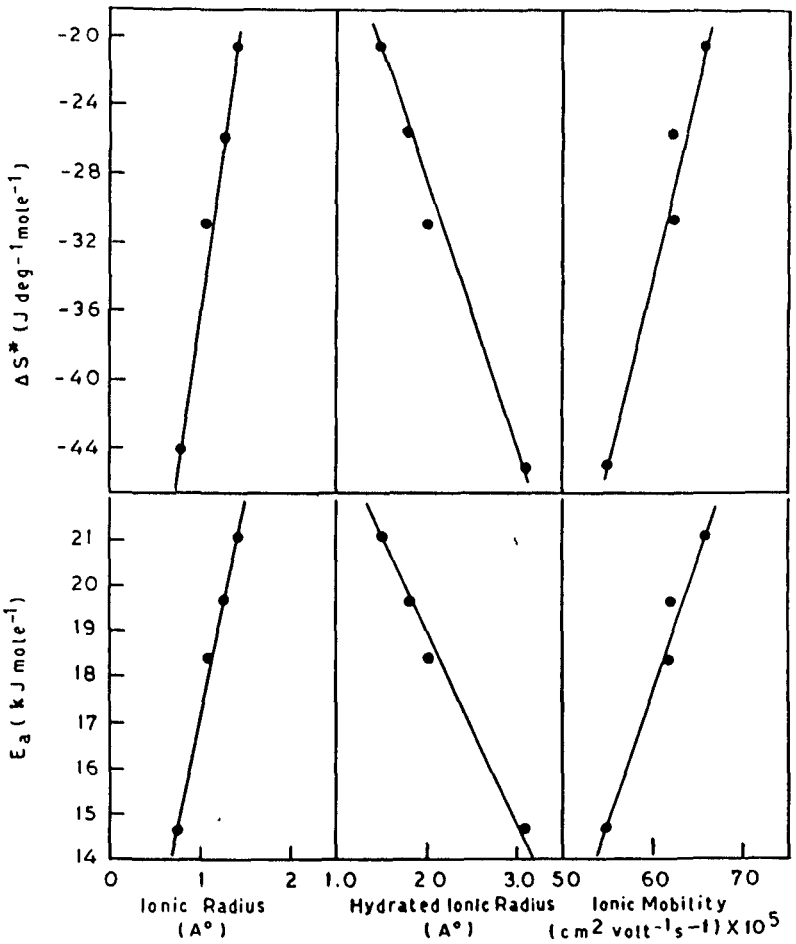


Fig. 3. Variation of E_a and ΔS^* with ionic radii, hydrated ionic radii and ionic mobilities of alkaline earth metals on zirconium(IV) arsenophosphate.

A comparison of the kinetic behaviour of various inorganic ion exchangers as shown in Fig. 4 indicates that the diffusion rate, activation energy and entropy of activation are, in general, lower on single salts [16—18] than on double salts [15, 19]. A positive entropy change on zirconium(IV) arsenosilicate probably accounts for the high efficiency of its columns [3].

ACKNOWLEDGEMENTS

The authors thank Professor M. Quereshi for research facilities. The financial assistance provided by the C.S.I.R., India, is gratefully acknowledged.

346

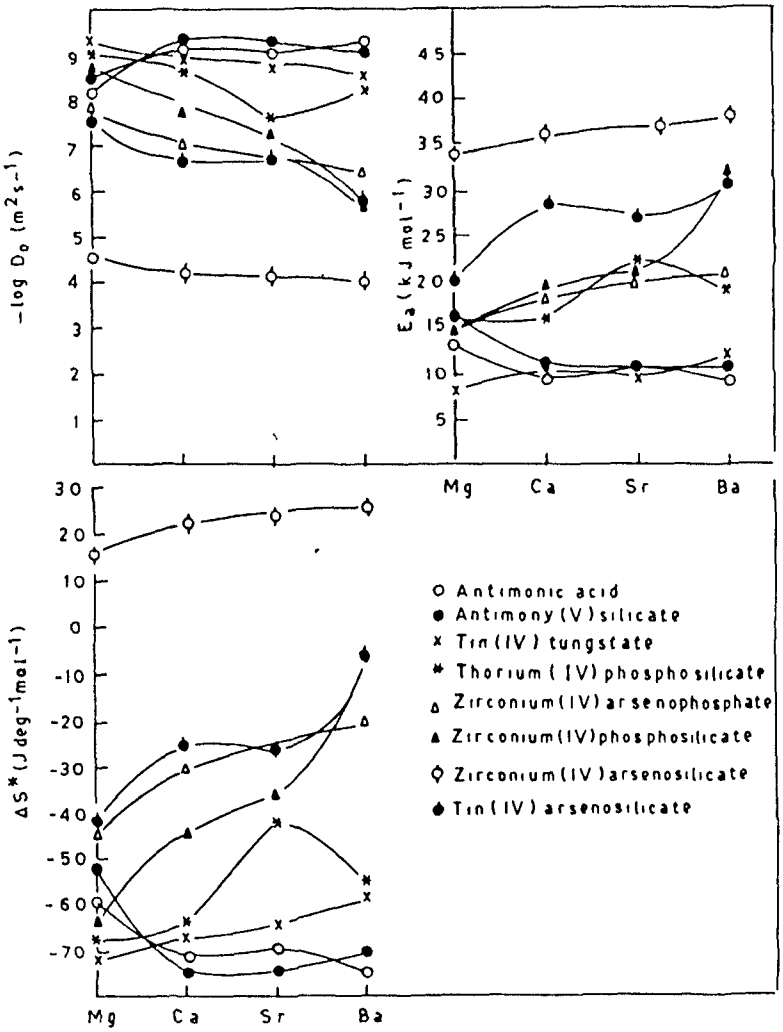


Fig 4 Diffusion coefficients, activation energies and entropies of activation for the alkaline earth metals exchanging with H(I) on different inorganic ion exchangers

REFERENCES

1 A Clearfield (Ed), Inorganic Ion Exchange Materials, CRC Press, Boca Raton, FL, 1982
2 K G Varshney, K Varshney and S Agrawal, Sep Sci Technol , 18 (1983) 905
3 K G Varshney, S Agrawal and K Varshney, Sep Sci Technol , 18 (1983) 59
4 K G Varshney, S Agrawal and K Varshney, Colloids Surfaces, 9 (1984) 189
5 K G Varshney, S Agrawal and K Varshney, Anal Lett , 16 (1983) 1381
6 K G Varshney, S Agrawal and K Varshney, J Liq Chromatogr , 7 (1981) 201
7 K G Varshney, S Agrawal and K Varshney, J Liq Chromatogr , 6 (1983) 1535
8 K G Varshney, S Agrawal, K Varshney, A Premadas, M S Rathi and P P Khanna, Talanta, 30 (1983) 955
9 K G Varshney, S Agrawal and K Varshney, Anal Lett , 16 (1983) 685

10 K.G. Varshney, S. Agrawal, K. Varshney and V. Saxena, Anal. Lett., in press.
11 K.G. Varshney and A. Premadas, Sep. Sci. Technol., 16 (1981) 793.
12 F. Helfferich, Ion Exchange, McGraw-Hill, New York, NY, 1962, Ch. 6.
13 R.M. Barrer, H.F. Bartholomew and L.V.C. Rees, J. Phys. Chem. Solids, 12 (1961) 21.
14 J. Lurie, Handbook of Analytical Chemistry, Mir Publishers, Moscow, 1978.
15 K.G. Varsheny, S. Agrawal and K. Varshney, Acta Chim. Hung., 116 (1984) 69.
16 K.G. Varshney and S. Rani, in F.G. Helfferich (Ed.), Reactive Polymers, Ion Exchangers, Sorbents, Elsevier, Amsterdam, in press.
17 K.G. Varshney and S. Rani, Indian J. Chem., 22A (1983) 657.
18 K.G. Varshney, A.A. Khan, K. Varshney and S. Agrawal, in E.P. Horwilz (Ed.), Solvent Extraction and Ion Exchange, Vol. 2, Dekker, New York, NY, 1984, p. 923.
19 K.G. Varshney, U. Sharma, S. Anwar and A.A. Khan, Indian J. Chem., 23A (1984) 152.

Reprinted from the *Indian Journal of Chemistry* Sec. A Vo. 20 No. 8 August 1981 pp. 841-843

3·5

Kinetics of Ag^+, Cu^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} & Y^{3+} Exchange in Sn(IV) Arsenophosphate

K. G. VARSHNEY* & A. PREMADAS

Chemistry Section, Z. H. College of Engineering & Technology, Aligarh Muslim University, Aligarh 202 001

Received 21 *October* 1980; *revised and accepted* 12 *January* 1981

The kinetics of exchange reactions of Ag^+, Cu^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Y^{3+} ions on Sn(IV) arsenophosphate have been studied at 23°, 30°, 40° and 60°C under the conditions favouring the particle diffusion mechanism only. At a concentration 0.1 *N*, rate of exchange has been found to be independent of the metal ion concentration. The diffusion coefficients, activation energies and entropies of activation have also been calculated.

KINETIC studies of synthetic inorganic ion exchangers have mostly been done on the crystalline and amorphous zirconium phosphate[1-5], zirconium oxide[6], tantalum arsenate[7], ceric phosphate[8] and ferric antimonate[9]. However, very little work has been reported[10,11] on the kinetic studies of double salts as ion exchangers. Amorphous Sn(IV) arsenophosphate has shown promising ion exchange properties and a high chemical and thermal stability[12]. Its affinity for metal ions is also found to be high[13]. In order to understand the mechanism of ion exchange in double salts, Sn(IV) arsenophosphate has, therefore, been selected for the kinetic studies of some metal ions.

Stannic chloride pentahydrate (U.S.S.R. product), disodium arsenate heptahydrate (Reidel, Germany) and trisodium orthophosphate (BDH) were used in the present studies. Other reagents and chemicals were either BDH or E. Merck products of AR grade.

An electric, temperature-controlled SICO (India) shaker was used for experimental studies.

Synthesis of Sn(IV) arsenophosphate — It was synthesized by mixing 0.1*M* solutions of stannic chloride, sodium arsenate and trisodium orthophosphate in the ratio 1:1:1 (v/v). The *p*H of the resultant gel was fixed at ~1 by adding nitric acid with constant stirring. After keeping it for 24 hr at room temperature, the gel was filtered through a Whatman No. 3 filter paper, washed with demineralised water (DMW) and then dried in an air oven at 40°C. After complete drying the product was immersed in DMW to form small granules. The particles were converted into the H^+ form by treating them with 2*M* HNO_3 for 24 hr, with occasional shaking, intermittently replacing the acid. The excess acid was finally washed out and the product dried at 40°C. The Na-ion exchange capacity of the dried material was found to be 1.75 meq/g.

Kinetic measurements — The rates of exchange of metal ions were determined by the limited bath technique[7]. The ion exchanger was ground and sieved into the following different sizes by using the U.S. standard mesh sieves : 60-100, 100-150, 150-200 and 200-250. Particles of mean radii 99.7 μm (60-100 mesh size) were generally used in the present studies unless stated otherwise. Fractions (20 ml) of the metal ion solutions (0.1 *N*) of constant ionic strength were shaken with exchanger (0.2 g) in a temperature-controlled shaker (0.5°C accuracy) *at various temperatures (23°, 30°, 40° and 60°C) in* the glass-stoppered conical flasks for different time intervals. The supernatant liquid was removed immediately by filtration through Whatman No. 4 filter paper and the volume was made up to 50 ml with DMW. The solution was then analysed quantitatively for the metal ion present, Cu^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Y^{3+} were determined with EDTA[14], while Ag^+ was determined titrimetrically by the thiocyanate method[15].

A study of the concentration effect ($1\times10^{-3}N$ to $1\times10^{-1}N$) on the rate of exchange for the Cu^{2+}-H^+ exchange at 30°C shows that at concentration $< 3\times10^{-3}N$, the initial rate of exchange is proportional to $[Cu^{2+}]$. At concentrations $>3\times10^{-3}N$, it is found to be independent of the metal ion concentration. Further, the *Bt* versus time plots for the concentrations ranging from $3\times10^{-3}N$ to $5\times10^{-3}N$ are not the good straight lines upto the maximum exchange. This may be due to both the particle and film diffusion phenomena taking place in this range of concentrations. However, at a concentration $>5\times10^{-3}N$ the *Bt* varies linearly with time and the straight lines obtained pass through the origin confirming a true particle diffusion phenomenon. Thus, for a high concentration of metal ion (0.1 *N*), a relatively large particle size of the exchanger and under vigorous shaking, the in-going ions may displace almost entirely the other ions in the exchanger at equilibrium. The extent of reaction *F* is expressed as,

$$F = \frac{\text{the amount of exchange at time t}}{\text{the amount of exchange at infinite time}}$$

Now, in the present case $CV >> \bar{C}\bar{V}$ where C is the concentration of metal ion in the solution phase, V is the volume of the solution, $\bar{C}$ is the concentration of the metal ion in the exchanger phase, and $\bar{V}$ is the volume of the exchanger. Thus, although the system is, in principle, a limited bath, the equation applicable to the infinite bath can be used in this case also as also verified by Reichenberg[16], Helfferich[17] and Blickenstaff[18,19] in their studies.

$$\text{Hence, } F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2\,Bt) \qquad \ldots(1)$$

where $B = \frac{\pi^2}{r^2} D_i$ ...(2)

r = radius of the particle and D_i = the effective diffusion coefficient of the two ions undergoing exchange within the exchanger. Values of Bt as a function of F may be calculated as given by Reichenberg[16]. The Bt versus t plots, at four selected temperatures, are shown in Fig. 1, for Cu^{2+} ion (C 0.1 N). Similar curves are obtained for Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Y^{3+}. At higher temperatures, the rate of exchange is faster and attains the equilibrium more quickly. The B values calculated from these plots are given in Table 1.

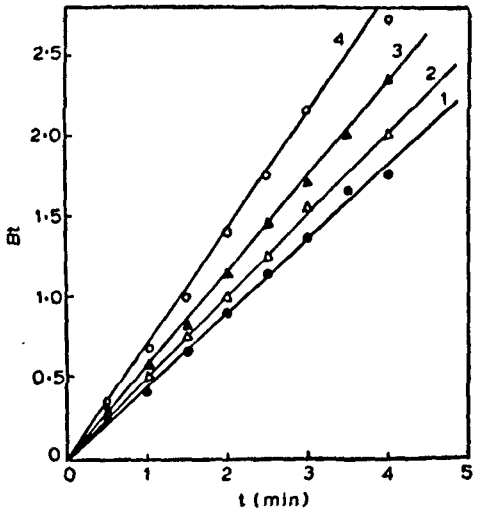


Fig. 1 — Influence of temperature on the rate of exchange for Cu^{2+} using Sn(IV) arsenophosphate (H^+) [1, 23°C; 2, 30°C; 3, 40°C; 4, 60°C]

The effect of the particle size upon the rate of exchange was studied for the exchange of Cu^{2+} ion upon the exchanger particle of different mean radii (Fig. 2). The results show that the exchange rate increases with the decrease in the particle size which is in agreement with the fundamental condition of the particle diffusion.

Equation (2) was used for the calculation of diffusion coefficient (D_i). A plot of log D_i versus 1/T is a straight line for all the metal ions used, as shown in Fig. 3. The values of E_a (energy of activation) were obtained by applying the Arrhenius equation $D_i = D_0 \exp(-E_a/RT)$. As Table 2 suggests, E_a increases with a decrease in the hydrated radii for alkaline earths. This behaviour is similar to that of the monovalent cations migrating through analcite[20]. We may conclude therefore that the hydrated ionic radii contribute to the mechanism of exchange reaction in two ways : (a) by affecting the position of equilibrium, and (b) by affecting the rate of attainment of equilibrium. It indicates the feasibility of separating ions by exploiting difference in their rate of exchange on Sn(IV) arsenophosphate.

D_0 is related with the entropy of activation ($\triangle S^*$) as follows,

$D_0 = 2.72\, d^2\, kT/h \exp(\triangle S^*/R)$ ...(3)

TABLE 1 — B VALUE AS A FUNCTION OF TEMPERATURE AND PARTICLE SIZE

Metal ion	r^* (μm)	B(sec^{-1})			
		23°C	30 C	40°C	60°C
Ag^+	99.7	1.51×10^{-3}	1.62×10^{-3}	1.97×10^{-3}	2.45×10^{-3}
Cu^{2+}	99.7	7.41×10^{-3}	8.48×10^{-3}	9.37×10^{-3}	1.22×10^{-2}
Cu^{2+}	61.0	—	9.00×10^{-3}	—	—
Cu^{2+}	41.7	—	1.00×10^{-2}	—	—
Cu^{2+}	34.0	—	1.12×10^{-2}	—	—
Mg^{2+}	99.7	8.30×10^{-3}	8.70×10^{-3}	9.03×10^{-3}	1.10×10^{-2}
Ca^{2+}	99.7	8.40×10^{-3}	9.00×10^{-3}	9.60×10^{-3}	1.23×10^{-2}
Sr^{2+}	99.7	9.80×10^{-3}	1.12×10^{-2}	1.25×10^{-2}	1.53×10^{-2}
Ba^{2+}	99.7	1.03×10^{-2}	1.25×10^{-2}	1.43×10^{-2}	1.70×10^{-2}
Y^{3+}	99.7	6.02×10^{-3}	6.34×10^{-3}	7.21×10^{-3}	8.33×10^{-3}

r^*mean radius of the particle.

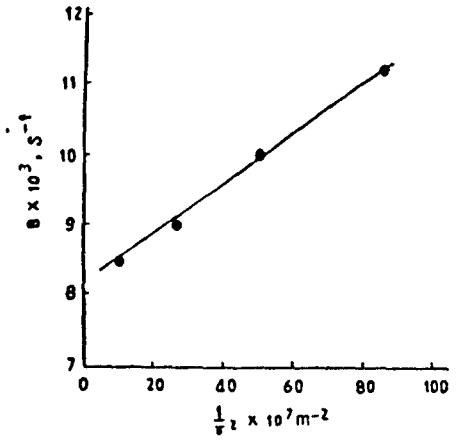


Fig. 2 — Plot of B against $1/r^2$ for Cu^{2+} at 30°C.

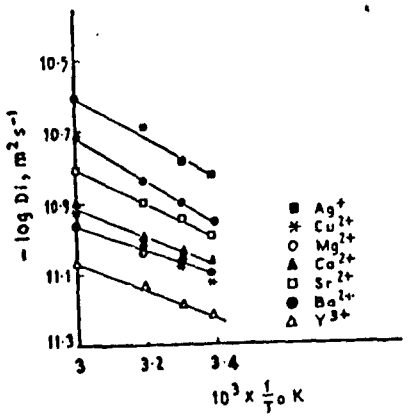


Fig. 3 — Plot of log Di against 1/T for different metal ions

where d is the ionic jump distance taken[21] as 5 Å, k is the Boltzmann constant and h is the Planck's constant, T is taken as 303°K. Table 2 summarizes the calculated values of $\triangle S^*$ which are negative as observed in tantalum arsenate[7] and ferric antimonate[9] also. A comparison of $\triangle S^*$ values for alkaline earths reveals that it increases with increasing ionic radii. The same conclusion was drawn by Freeman and Staimers[22] in Y-zeolite.

TABLE 2 — SELF-DIFFUSION COEFFICIENT, ENERGY OF ACTIVATION AND ENTROPY OF ACTIVATION OF CERTAIN METAL IONS ON Sn(IV) ARSENOPHOSPHATE (r^*=99.7 μm)

Migrating ion	Hydrated ionic radii (Å)	D_0 ($m^2\ s^{-1}$)	E_a ($KJ\ mol^{-1}$)	ΔS^* ($JK^{-1}\ mol^{-1}$)
Ag^+	—	1.11×10^{-9}	10.63	—68.68
Cu^{2+}	—	5.11×10^{-10}	10.30	—75.13
Mg^{2+}	3.10	1.49×10^{-10}	7.14	—85.38
Ca^{2+}	2.00	2.02×10^{-10}	7.82	—82.85
Sr^{2+}	1.80	4.56×10^{-10}	9.32	—76.08
Ba^{2+}	1.50	1.40×10^{-9}	11.88	—66.75
Y^{3+}	—	1.25×10^{-10}	7.49	—86.83

The authors are thankful to Prof. M. Qureshi and Prof. W. Rahman for research facilities and to the CSIR, New Delhi for financial assistance to one of them (A. Premadas).

References

1. RUVARAC, A. & VESELEY, V., *J. inorg. nucl. Chem.*, **32** (1970), 3939.
2. RUVARAC, A. L., *J. Chromatogr.*, **60** (1971), 235.
3. CLEARFIELD, A. & MEDINA, A. S., *J. inorg. nucl. Chem.*, **32** (1970), 2775.
4. ALBERTI, G., BERTRAMI, R., CASCOILA, M., COSTANTIONO, U. & GUPTA, J. P., *J. inorg. nucl. Chem.*, **38** (1976), 843.
5. NANCOLLAS, G. H. & PATERSON, R., *J. inorg. nucl. Chem* **22** (1961), 259.
6. RUVARAC, A. L. & TRTANJ, M. I., *J. inorg. nucl., Chem.*, **34** (1972), 3893.
7. RAWAT, J. P. & THIND, P. S., *J. phys. Chem.*, **80** (1976), 1384.
8. HERMAN, R. G. & CLEARFIELD, A., *J. inorg. nucl. Chem.*, **38** (1976), 853.
9. RAWAT, J. P. & SINGH, D. K., *J. inorg. nucl. Chem.*, **40** (1978), 897.
10. CHOUDHURI, D. & MUKHERJEE, S. K., *J. inorg. nucl. Chem.*, **33** (1971), 1933.
11. SINGH, N. J., MATHEW, J. & TANDON, S. N., *J. phys. Chem.*, **84** (1980), 21.
12. VARSHNEY, K. G. & KHAN, A. A., *J. inorg. nucl. Chem.*, **41** (1979), 241.
13. VARSHNEY, K. G. & KHAN, A. A., *Talanta*, **25** (1978), 528.
14. REILLEY, C. N., SCHMID, R. W. & SADEK, F. S., *J. chem. Educ.*, **36** (1959), 555.
15. KOLTHOFF, I. M., SANDELL, E. B., MECHAN, E. J. & BRUCKENSTEIN, S., *Quantitative chemical analysis*, 4th edn (Macmillan company, London), 1952, 798.
16. REICHENBERG, D., *J. Am. chem. Soc.*, **75** (1953), 589.
17. HELFFERICH, F., *J. phys. Chem.*, **69** (1965), 1178.
18. BLICKENSTAFF, R. A., WAGNER, J. D. & DRANOFF, J. S., *J. phys. Chem.* **71** (1967), 1665.
19. BLICKENSTAFF, R. A., WAGNER, J. D. & DRANOFF, J. S., *J. phys. Chem.* **71** (1967), 1610.
20. BARRER, R. M. & REER, L. V. C., *Nature*, **187** (1960), 768.
21. BARRER, R. M., BARTHOLOMEW, R. F. & REES, L. V. C., *J. phys. Chem. Solids*, **12** (1961), 21.
22. FREEMAN, D. C. & STAIMERS, D. N., *J. chem. Phys.*, **35** (1961), 799.

React. Kinet. Catal. Lett., Vol. 40, No. 2, 319-325 (1989)

3·6 EVALUATION OF THE ENERGY AND ENTROPY OF ACTIVATION FOR THE FORWARD AND REVERSE EXCHANGES OF ALKALINE EARTH METALS ON ANTIMONY(V) ARSENOPHOSPHATE CATION EXCHANGERS-A KINETIC APPROACH

K.G. Varshney, A.A. Khan and Ashfaq Rabbani Khan
Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002, India

Received December 14, 1988
Accepted April 24, 1989

Forward and reverse ion exchange kinetics have been studied on antimony(V) arsenophosphate for the Ba(II)-H^+, Ca(II)-H^+, Sr(II)-H^+ and Mg(II)-H^+ exchanges under conditions favoring a particle diffusion. On the basis of these studies various physical parameters have been evaluated, such as the diffusion coefficients, activation energies and entropies of activation.

Кинетику прямого о обратного ионного обмена исследовали на арсенофосфате сурьмы(V) для следующих пар: Ba(II)-H(I), Ca(II)-H(I), Sr(II)-H(I) и Mg(II)-H(I) в условиях, благоприятствующих диффузии частиц. Определяли различные физические параметры, такие как коэффициенты диффузии, энергии и энтропии активации.

INTRODUCTION

Energy and entropy of activation play a vital role in understanding the reactions occurring in a system. Recently, we have studied these parameters only for the forward processes

Akadêmiai Kiadó, Budapest

[1-4] on the basis of the Nernst-Planck equations [5,6] as against the old Bt criterion [7-11] proposed by Boyd et al. [12]. No studies have been made so far for the forward and reverse exchanges on inorganic ion-exchangers for alkaline earths. Only the Na^+-H^+ and K^+-H^+ exchanges have been studied earlier in these labs on antimony(V) silicate [13]. In order to extend such studies further the present work was undertaken, the results of which are summarized in the following pages. The matrix selected has been the antimony(V) arsenophosphate exchanger and the metal ions taken are the alkaline earths.

EXPERIMENTAL

All chemicals and reagents were of Analar grade. A water-bath incubator shaker having a temperature variation of ±0.5 °C was used in the equilibrium studies.

Synthesis of the Ion Exchange Material. Antimony(V) arsenophosphate was prepared as earlier [14].

Kinetic Measurements. Ion exchanger particles of mean radii 121 μm (50-72 mesh size) in H^+ form were used in this experiment. 20 ml fractions of the 0.05 M metal ion solution (Mg, Ca, Sr and Ba) were shaken with 200 mg of the exchanger in several stoppered conical flasks at the desired temperature (20, 30, 45 and 60 ±0.5 °C) for different time intervals. Determination of supernatant liquid were done by EDTA titrations. In the reverse process the exchanger was taken in the metal form and shaken with 20 ml of 0.1 M HNO_3. The supernatant liquid was titrated against a standard NaOH solution to find out the amount of the H^+ ions adsorbed on the exchanger.

RESULTS AND DISCUSSION

Kinetic measurements were performed on the surface of antimony(V) arsenophosphate under conditions favoring a particle diffusion-controlled ion exchange for forward and reverse exchanges of Mg(II)-H^+, Ca(II)-H^+, Sr(II)-H^+ and Ba(II)-H^+. The fractional attainment of equilibrium $U_{(\tau)}$ may be expressed as:

$$U_{(t)} = \frac{\text{degree of exchange at time t}}{\text{degree of exchange at equilibrium}}$$

Each value of $U_{(\tau)}$ has a corresponding value of τ (a dimensionless time parameter) obtained from our previous work [15] by substituting the various values in the following equation [16]

$$U_{(\tau)} = \{1-\exp[\pi^2 (f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2}$$

Plots of τ vs. t at the four different temperatures for metal(II)-H^+ and H^+-metal(II) exchanges at a concentration of 0.05 M (metal) and 0.1 M (hydrogen) are shown in Fig. 1. Straight lines passing through the origin confirm the particle diffusion phenomenon.

Slopes (S) of such lines for all the forward and reverse exchanges are given in Table 1 which are related to $\bar{D}_A$ as follows:

$$S = \frac{\bar{D}_A}{r_o^2}$$

Table 1

Slopes (S) of the various τ versus time plots for forward and reverse exchanges of alkaline earths on antimony(V) arsenophosphate

Migrating ion	Ion present in the ion exchanger	S (s^{-1})			
		20 °C	30 °C	45 °C	60 °C
Mg(II)	H^+	1.5×10^{-2}	1.9×10^{-2}	2.9×10^{-2}	4.5×10^{-2}
H^+	Mg(II)	1.75×10^{-2}	3.0×10^{-2}	3.87×10^{-2}	5.0×10^{-2}
Ca(II)	H^+	1.0×10^{-2}	1.5×10^{-2}	1.9×10^{-2}	2.5×10^{-2}
H^+	Ca(II)	1.0×10^{-2}	1.62×10^{-2}	2.25×10^{-2}	2.87×10^{-2}
Sr(II)	H^+	0.85×10^{-2}	1.05×10^{-2}	1.35×10^{-2}	1.9×10^{-2}
H^+	Sr(II)	1.40×10^{-2}	2.20×10^{-2}	3.8×10^{-2}	5.0×10^{-2}
Ba(II)	H^+	0.35×10^{-2}	0.55×10^{-2}	0.80×10^{-2}	1.15×10^{-2}
H^+	Ba(II)	1.4×10^{-2}	1.8×10^{-2}	2.7×10^{-2}	3.8×10^{-2}

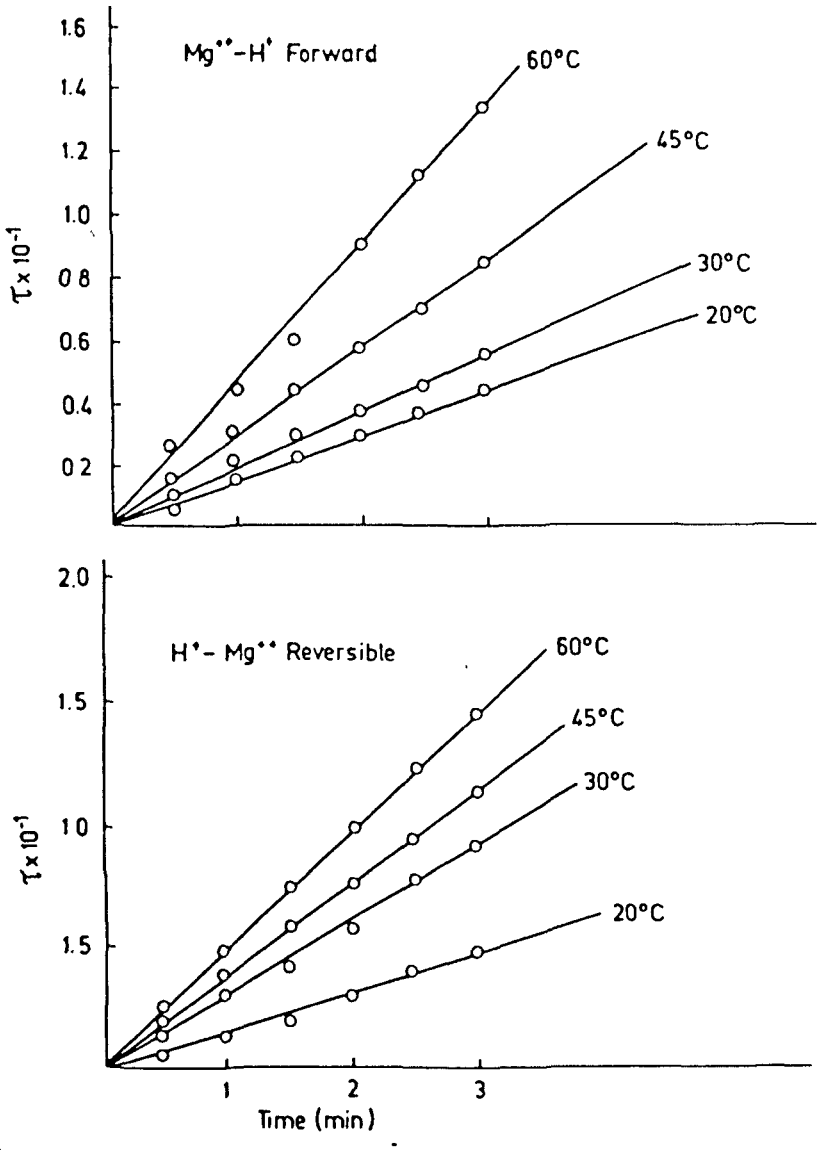


Fig. 1. Plots of τ versus time for Mg(II)-H^+ and H^+-Mg(II) exchange on antimony(V) arsenophosphate at different temperatures

The value of log $\bar{D}_A$ obtained by this equation are plotted

against $\frac{1}{T}$, for forward and reverse exchanges shown justifying the validity of the Arrhenius equation

$$\bar{D}_A = D_o \exp(-E_a/RT)$$

The pre-exponential constants, D_o, are obtained by extrapolating these curves observing the intercept at the Y axis, and taking the value of $\bar{D}_A$ at 273 K.

The energy of activation (E_a) values can be calculated by the use of the above equation. While the entropy of activation (ΔS^*) is obtained by using the following equation

$$D_o = 2.72\, d^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right)$$

where k and h are the Boltzman and Planck constants, respectively, d is the ionic jump distance taken [17] as 0.5 nm; R is the gas constant and T is taken as 273 K. The values of D_o, E_a and ΔS^* are summarized in Table 2. As the results show, the

Table 2

D_o, energy of activation and entropy of activation of alkaline earths for forward and reverse exchanges on antimony(V) arsenophosphate

Migrating ion	Ion present in the exhanger	Ionic mobility ($10^8 m^2 V^{-1}$)	Ionic radii (Å)	Hydrated ionic radii (Å)	D_o ($m^2 s^{-1}$)	E_a (kJ mol^{-1})	ΔS^* (Jk^{-1} mol^{-1})
Mg(II)	H^+	5.5	0.78	3.1	8.41×10^{-7}	19.85	-12.69
H^+	Mg(II)	-	-	-	5.6×10^{-6}	23.64	+3.06
Ca(II)	H^+	6.2	1.06	2.0	7.07×10^{-7}	20.24	-14.13
H^+	Ca(II)	-	-	-	4.73×10^{-6}	24.82	+1.66
Sr(II)	H^+	6.2	1.27	1.8	5.01×10^{-7}	24.95	-16.99
H^+	Sr(II)	-	-	-	7.90×10^{-6}	25.34	+5.93
Ba(II)	H^+	6.6	1.43	1.5	17.78×10^{-7}	25.08	-6.46
H^+	Ba(II)	-	-	-	3.16×10^{-6}	22.86	-1.68

negative values of ΔS^* indicate that the ion exchange process is more feasible on antimony(V) arsenophosphate when the exchanger phase is in H^+ form and exchanged by a metal ion. For a forward exchange, there is a decrease in the ΔS^* values with the decrease in the hydrated radii except for the H^+-Ba(II) ex-

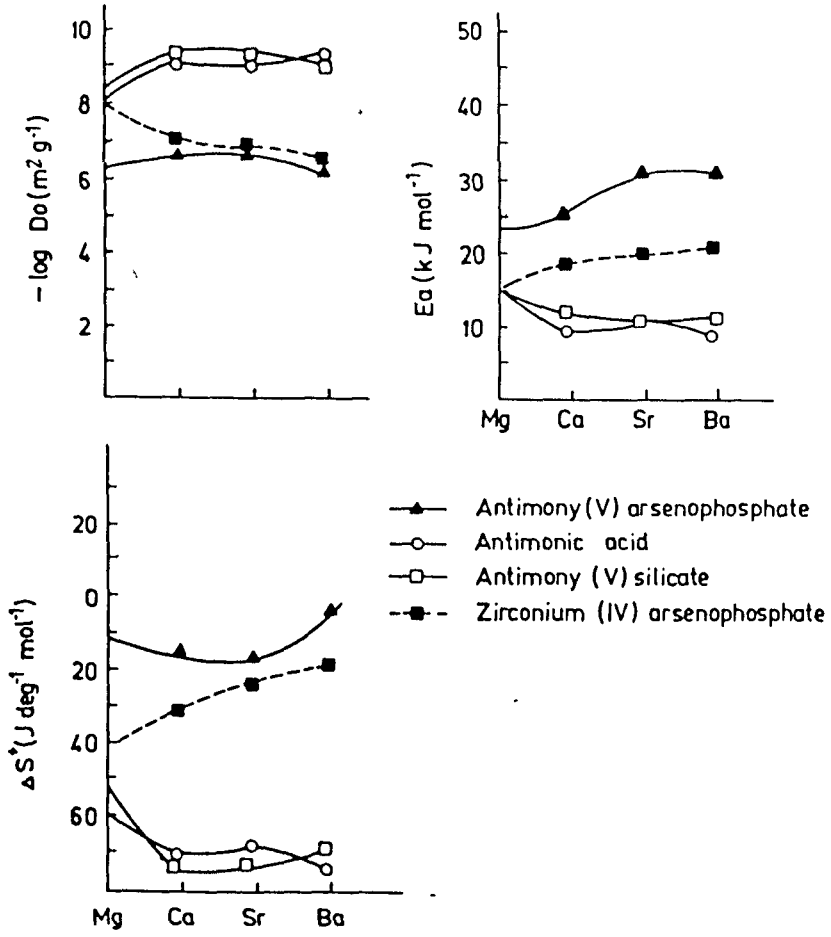


Fig. 2. Diffusion coefficients, activation energies and entropies of activation for alkaline earth metals exchanging with H^+ on different inorganic ion exchangers

change showing a greater exchange in that order. For the reverse exchange, however, the trend is not certain.

A comparison of kinetic behavior of various inorganic ion exchangers in Fig. 2 indicates higher values of ΔS^* and E_a for antimony(V) arsenophosphate as compared to other materials of this class.

Acknowledgements. The authors thank Professor K.T. Nasim for research facilities. The financial assistance provided by the C.S.I.R., India is gratefully acknowledged.

REFERENCES

1. K.G. Varshney, S. Agrawal, K. Varshney: Acta Chim. Acad. Sci.Hung. 116, 69 (1984)
2. K.G. Varshney, Sima Rani: Ind.J.Chem., 22A, 657 (1983)
3. K.G. Varshney, Sanjay Agrawal, Kanak Varshney: Coll.Surf., 13, 341 (1985)
4. K.G. Varshney, Sima Rani: Reactive Polymers, 3, 231 (1985)
5. W.Z. Nernst: Phys.Chem., 2, 613 (1888); 4, 729 (1889)
6. M. Planck: Ann.Phys.Chem., 39, 161 (1890)
7. J.P. Rawat, P.S. Thind: J.Phys.Chem., 80, 1384 (1976)
8. A. Dyer, J.S. Gill: J.Inorg.Nucl.Chem., 39, 665 (1977)
9. K. Bunzl: J.Inorg.Nucl.Chem., 39, 1049 (1977)
10. J.P. Rawat, D.K. Singh: J.Inorg.Nucl.Chem., 40, 897 (1978)
11. K.G. Varshney, A. Premadas: Ind.J.Chem., 20(A), 841 (1981)
12. G.E. Boyd, A.W. Adamson, L.S. Myers: J.Am.Chem.Soc., 69, 2836 (1947)
13. K.G. Varshney, A.A. Khan, S. Rani: Coll.Surf., 25, 131 (1987)
14. K.G. Varshney, A.A. Khan, A.R. Khan: Bull.Chem.Soc.Jpn., 61, 3693 (1988)
15. K.G. Varshney, Kanak Varshney, Sanjay Agrawal: Coll.Surf., 18, 67 (1986)
16. F. Helfferich: Ion Exchange, Ch. 6. McGraw-Hill, New-York 1962.
17. R.M. Barrer, R.F. Bartholomew, L.V.C. Rees: Phys.Chem. Solids, 12, 21 (1961)

Acta Chimica Hungarica 116 (1), pp. 103–109 (1984)

3.7 KINETICS OF EXCHANGE OF TRANSITION METALS ON ZIRCONIUM(IV) AND THORIUM(IV) PHOSPHOSILICATE CATION EXCHANGERS

K. G. VARSHNEY* and U. SHARMA

(Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh-202001, India)

Received April 2, 1983
In revised form June 17, 1983
Accepted for publication July 13, 1983

Kinetics of the exchange reactions of Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions on Zr(IV) and Th(IV) phosphosilicate cation exchangers has been studied at 25, 32, 50 and 65 °C under the conditions favourable to the particle diffusion mechanism only and the rate of exchange has been found to be independent of the metal ion concentration at and above 0.01 *M* in aqueous medium on both the materials. Various kinetic parameters such as self-diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation (ΔS^*) have been calculated which are useful for predicting the ion exchange phenomenon taking place.

Introduction

Inorganic ion exchangers are generally used for the metal separations. They are superior to the organic resins as they are resistant to heat and radiations. To understand the mechanism underlying in an ion exchange process its kinetic studies are essential which have been done mostly on the crystalline and amorphous zirconium phosphate [1—5], zirconium oxide [6], tantalum and tin arsenates [7, 8], ceric phosphate [9] and zirconium, iron and tin antimonates [10—12]. Moreover, these studies are based on the old Bt criterion [13] which is not very useful for an ion exchange process because of the different effective diffusion coefficients taking part in such a case. Here, the Nernst—Planck [14, 15] equations are more appropriate. Since the kinetic studies are rarely made [16—18] on double salts, the following pages summarize our study on zirconium(IV) and thorium(IV) phosphosilicates (ZPS and TPS) as cation exchangers, taking transition metal ions as exchanging species with H^+ ions.

Experimental

Reagents and chemicals

Zirconyl chloride and thorium nitrate were of B.D.H. (England) while sodium silicate was a Riedel (DEHAENAG, Seelze Hannover) product. All other reagents and chemicals were of AnalaR grade.

* To whom correspondence should be addressed

Apparatus

A water bath incubator shaker having a temperature variation of ±0.5 °C was used for the equilibrium studies.

Synthesis of the ion exchange materials

To a definite volume of a 0.1 *M* sodium silicate ($Na_2SiO_3 \cdot 3H_2O$) solution *conc.* HCl (5 mL per 100 mL Na-silicate solution) and a definite volume of 0.1 *M* zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) solution were added. The pH of the mixture was made 9–10 by adding NH_4OH and the resultant slurry was allowed to stand overnight. It was filtered, washed with DMW and mixed with a fixed volume of a H_3PO_4–HNO_3 mixture (1 *M* in terms of each acid). The gel thus obtained was kept overnight, filtered out, washed thoroughly with DMW, dried at 45 °C in an air oven and was cracked in DMW to form small granules. The granules were then placed in 1 *M* HNO_3 to convert them into the H^+-form and were finally washed and dried at 45 °C before use for further study. TPS was prepared in a similar manner by taking thorium nitrate $Th(NO_3)_4 \cdot 6H_2O$ instead of zirconium oxychloride. The Na^+-ion exchange capacities of these materials (ZPS and TPS) were found to be 2.19 and 1.66 meq/dry g, respectively.

Kinetic measurements

The rates of exchange of metal ions were determined by the limited bath technique. 20 mL fractions of the 0.01 *M* metal ion solutions of the divalent transition metals (Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}) were shaken with 200 mg of the exchanger beads (mean radius 120 μm; 100–150 mesh size) in some stoppered conical flasks at the desired temperature (25, 32, 50 and 65 °C ±0.5 °C) for different time intervals as mentioned in Fig. 2. Supernatant liquid was immediately removed by filtering through a Whatman No. 1 filter paper and the determinations were done by EDTA titrations [19] using Eriochrome Black T as an indicator.

Results and Discussion

A study of the concentration effect on the rate of Mn^{+2}—H^+ exchange at 25 °C shows that at concentrations $\leq$0.01 *M* the initial rate of exchange is proportional to $[Mn^{2+}]$. At concentrations $\geq$0.01 *M* it is found to be independent of the metal ion concentration. Under the conditions of a particle diffusion control, a relatively large particle size of the exchanger and vigorous shaking the fractional attainment of equilibrium may be given as,

$$U(\tau) = \frac{\text{the total amount of exchange at time '}t\text{'}}{\text{the amount of exchange at infinite time}} \qquad (1)$$

A plot of $U(\tau)$ versus t (Fig. 1) for Mn^{2+} ion on ZPS and TPS indicates that the fractional attainment of equilibrium is faster at a higher temperature, an observation analogous to the other materials of this class. Although this is a limited bath system, the equation applicable to an infinite bath can be used here because $CV \gg \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and exchanger phases, respectively. V and $\bar{V}$ are the volumes of these two phases. The Nernst—Planck equations can be solved with some additional assumptions [20], which are valid for inorganic ion exchangers as the swelling changes and the specific interactions are not significant in this

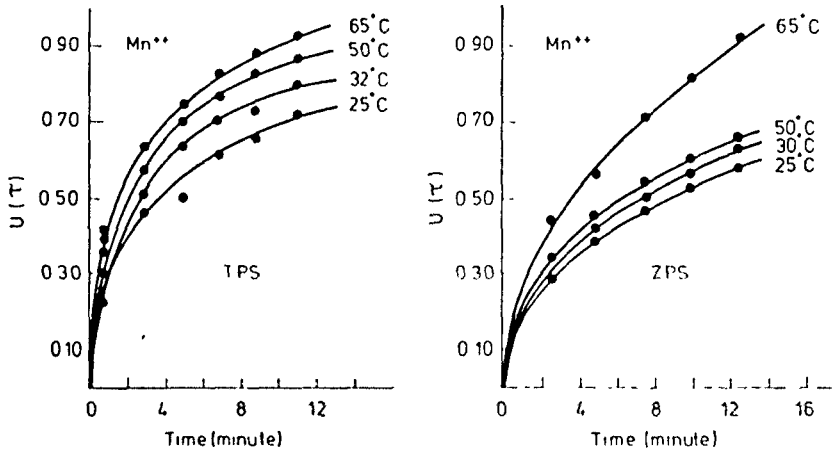


Fig. 1

case. As a result we obtain a coupled interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions A and B in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$ the interdiffusion coefficient assumes the values $\bar{D}_A$, A being the counter ion initially present in the ion exchanger phase. Since in the present case the exchanger is taken in H^+ form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Thus, on the basis of the Nernst—Planck equations

$$U(\tau) = 1 - \exp\left\{[\pi^2(f_1(\alpha)\,\tau + f_2(\alpha)\,\tau^2 + f_3(\alpha)\,\tau^3)]\right\}^{\frac{1}{2}} \tag{2}$$

where

$$\tau = \frac{\bar{D}_H t}{r_0^2}$$

and the mobility ratio $\alpha = \dfrac{\bar{D}_H}{\bar{D}_M}$, r_0 particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leq \alpha < 20$ and $Z_H/Z_M = 1/2$ as in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed [21] as:

$$f_1(\alpha) = \frac{1}{0.64 + 0.36\,\alpha^{0.668}} \tag{a}$$

$$f_2(\alpha) = \frac{1}{0.96 - 2.0\,\alpha^{0.4635}} \tag{b}$$

and

$$f_3(\alpha) = \frac{1}{0.27 + 0.09\,\alpha^{1.14}} \tag{c}$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained on solving equation (2) by graphical method. The plots of τ vs. t at the four different temperatures (Fig. 2) on ZPS and TPS for the Mn^{2+} ions are shown at a concentration 0.1 M which are straight lines passing through the origin. It confirms a particle diffusion controlled phenomenon. The slopes (S) of such lines for all the four transition metals on ZPS and TPS are given in Table I, which are related with $\bar{D}_H$ as follows:

$$S = \frac{\bar{D}_H}{r_0^2} \tag{3}$$

The plots of $-\log \bar{D}_H$ vs. $1/T$ are straight lines as shown in Fig. 3, thus varifying the Arrhenius relation:

$$\bar{D}_H = D_0 e^{(E_a/RT)} \tag{4}$$

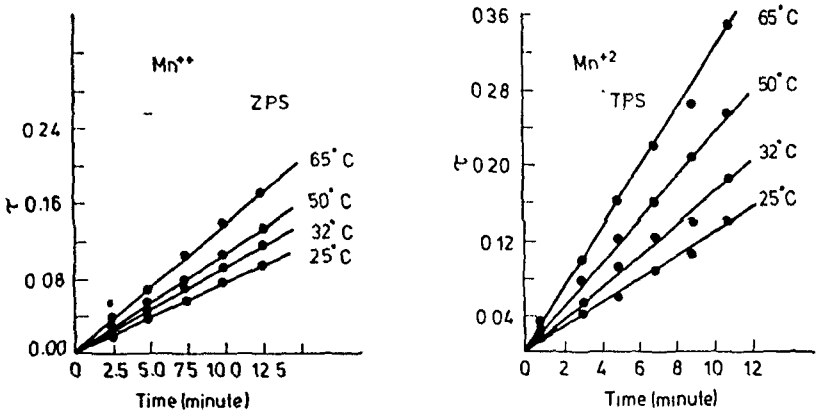


Fig. 2

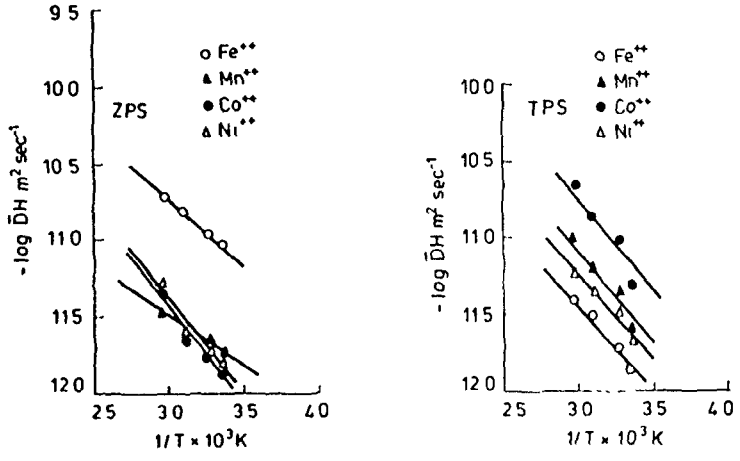


Fig. 3

Table I

Slopes of the various τ versus time plots for transition metals on Zr(IV) and Th(IV) phosphosilicates

Migrating ion	Slopes (s^{-1})							
	On ZPS				On TPS			
	25 °C	35 °C	50 °C	65 °C	25 °C	35 °C	50 °C	65 °C
Mn^{2+}	1.27×10^{-4}	1.55×10^{-4}	1.77×10^{-4}	2.44×10^{-4}	1.83×10^{-4}	3.16×10^{-4}	4.16×10^{-4}	5.33×10^{-4}
Fe^{3+}	6.38×10^{-4}	7.77×10^{-4}	1.11×10^{-4}	14.44×10^{-4}	1.00×10^{-3}	1.33×10^{-4}	2.16×10^{-4}	2.66×10^{-4}
Co^{2+}	1.00×10^{-4}	1.27×10^{-4}	1.72×10^{-4}	3.11×10^{-4}	3.33×10^{-4}	5.00×10^{-4}	9.44×10^{-4}	16.11×10^{-4}
Ni^{2+}	1.11×10^{-4}	1.33×10^{-4}	1.72×10^{-4}	3.33×10^{-4}	1.66×10^{-4}	2.33×10^{-4}	3.16×10^{-4}	4.00×10^{-4}

Table II

Self-diffusion coefficient, energy of activation and entropy of activation of transition metals on Zr(IV) and Th(IV) phosphosilicates

Migrating ion	Ionic mobility (m^2 volt^{-1} s^{-1})	Ionic radii (nm)	D_o, E_a and ΔS^* values					
			On ZPS			On TPS		
			D_o ($m^2 s^{-1}$)	E_a (kJ mole^{-1})	ΔS^* (JK^{-1} mole^{-1})	D_o ($m^2 s^{-1}$)	E_a (KJ mole^{-1})	ΔS^* (JK^{-1} mole^{-1})
Mn^{2+}	55×10^{-9}	9.1×10^{-2}	3.55×10^{-10}	13.07	−77.29	2.51×10^{-8}	22.21	−47.88
Fe^{2+}	54×10^{-9}	6.7×10^{-2}	8.41×10^{-9}	16.85	−31.83	5.01×10^{-9}	19.86	−55.28
Co^{2+}	55×10^{-9}	8.2×10^{-2}	1.88×10^{-8}	23.52	−44.27	6.68×10^{-8}	22.60	−33.74
Ni^{2+}	52×10^{-9}	7.8×10^{-2}	1.99×10^{-8}	23.25	−43.79	1.00×10^{-8}	20.51	−49.53

D_0 is then obtained by extrapolating these lines and observing the intercepts at the origin. E_a values are then calculated from equation (4) putting the value of $\bar{D}_H$ corresponding to the T value as 273 °K in the graph. Finally ΔS^* values are obtained from the expression:

$$D_0 = 2.72\, d^2 \frac{kT}{h} \exp\left(\Delta S^*/R\right) \qquad (5)$$

where d is the ionic jump distance [22] taken as 0.5 nm and k and h are the Boltzmann and Planck constants, respectively. T is taken as 273 °K. The values of D_0, E_a and ΔS^* are summarized in Table II.

The authors are thankful to Prof. Mohsin Qureshi for the research facilities and to the C.S.I.R., India for the financial assistance.

REFERENCES

[1] Ruvarac, A. L., Veseley, V.: J. Inorg. Nucl. Chem., **32**, 3939 (1970)
[2] Ruvarac, A. L.: J. Chromatogr., **60**, 235 (1971)
[3] Clearfield, A., Medina, A. S.: J. Inorg. Nucl. Chem., **32**, 2775 (1970)
[4] Alberti, G., Costantino, U., Bertrami, R., Cascoila, M., Gupta, J. P.: J. Inorg. Nucl. Chem., **38**, 843 (1976)
[5] Nancollas, G. H., Paterson, R.: J. Inorg. Nucl. Chem., **22**, 259 (1961)
[6] Ruvarac, A. L., Trtanj, M. I.: J. Inorg. Nucl. Chem., **34**, 3893 (1972)
[7] Rawat, J. P., Thind, P. S.: J. Phys. Chem., **80**, 1384 (1976)
[8] Rawat, J. P., Khan, M. A.: J. Inorg. Nucl. Chem., **42**, 905 (1980)
[9] Herman, R. G., Clearfield, A.: J. Inorg. Nucl. Chem., **38**, 853 (1976)
[10] Methew, J., Tandon, S. N.: Can. J. Chem., **55**, 3857 (1977)
[11] Rawat, J. P., Singh, D. K.: J. Inorg. Nucl. Chem., **40**, 897 (1978)
[12] Singh, N. J., Tandon, S. N., Ind. J. Chem., **19A**, 416 (1980)
[13] Boyd, G. E., Adamson, A. W., Myers, L. S.: J. Am. Chem. Soc., **69**, 2836 (1947)
[14] Nernst, W. Z.: Physik Chem., **2**, 613 (1888); **4**, 129 (1889)
[15] Planck, M.: Ann. Phys. Chem., **39**, 161 (1890)
[16] Choudhuri, D., Mukherjee, S. K.: J. Inorg. Nucl. Chem., **33**, 1933 (1971)
[17] Singh, N. J., Mathew, J., Tandon, S. N.: J. Phys. Chem., **84**, 21 (1980)
[18] Varshney, K. G., Permadas, A.: Ind. J. Chem., **20A**, 841 (1981)
[19] Reilley, C. N., Schmid, R. W. E.: J. Chem. Educ., **36**, 555 (1959)
[20] Helfferich, F.: Ion-Exchange, McGraw-Hill Book Company, New York, p. 268. (1962)
[21] Helfferich, F.: Ion-Exchange, Mc Graw-Hill Book Company, New York, p. 271 (1962)
[22] Barrer, R. M., Bartholomew, R. F., Rees, L. V. C.: J. Phys. Chem. Solids, **12**, 21 (1961)

Colloids and Surfaces, 9 (1984) 189—197
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

3.8

ION-EXCHANGE KINETICS OF SOME METAL POLLUTANTS AND THEIR SEPARATION ON ZIRCONIUM(IV) PHOSPHO- AND SILICO-ARSENATE CATION EXCHANGERS

KRISHNA GOPAL VARSHNEY, SANJAY AGRAWAL and KANAK VARSHNEY

Analytical Laboratories, Chemistry Section, Z.H. College of Engineering & Technology, Aligarh Muslim University, Aligarh 202 001 (India)

(Received 29 July 1983; accepted in final form 4 October 1983)

ABSTRACT

Exchange kinetics of some polluting metal ions such as Mn(II), Fe(II), Co(II), Ni(II), Zn(II) and Cd(II) has been studied on zirconium(IV) phospho- and silico-arsenates, apply ing an approach based on the Nernst—Planck equations. As a result, some kinetic and thermodynamic parameters like diffusion coefficients, activation energies, and entropies of activation have been evaluated under the conditions favouring a particle diffusion-controlled mechanism. The theoretical predictions derived from these studies have been correlated with the practically achieved separations of cadmium(II) from some metals mentioned above.

INTRODUCTION

Zirconium(IV) phospho- and silico-arsenates have been synthesized in these laboratories [1, 2] showing excellent chemical stability and ion-exchange behaviour. They are highly selective for the heavy metals like iron manganese, cobalt, nickel, cadmium, lead, zinc and copper, which are hazard ous to health when adsorbed by the body beyond certain limits. Their utility has also been explored [2—6] in various fields including the analysis of rocks, alloys and drugs and water purification. Kinetic study of the ion exchange process occurring on the surface of such materials is important for their economic and industrial employment. We have earlier made such a study on some inorganic ion exchangers [7—10] applying a new approach based on the Nernst—Planck equations [11, 12] replacing the old "Bt criterion" [13—20], which is useful only for the ions having similar effective diffusion co efficients, i.e. for an isotopic exchange. In an ion-exchange process the fluxes of two different ionic species are coupled with one another [21] and, therefore, a single diffusion coefficient cannot describe the actual process. In the present paper, we have made an effort to understand the mechanism of the metal uptake by the phospho- and silico-arsenates of zirconium(IV) in aqueous media containing some heavy metal pollutants and to correlate the theoretical predictions with the practically achieved separations.

0166-6622/84/$03.00

MATERIALS AND METHODS

Reagents and chemicals

Zirconyl chloride, trisodium orthophosphate, disodium arsenate and arsenic acid used in this study were obtained either from the B.D.H., Poole (U.K.) or E. Merck (Darmstadt, F.R.G.). Sodium silicate was a Riedel (DEHAENAG, Seelze Hannover, F.R.G.) product and all other reagents and chemicals were of AnalaR grade.

Apparatus

A waterbath incubator shaker having a temperature variation of ± 0.5°C was used for the equilibrium studies.

Synthesis of the ion-exchange materials

Zirconium(IV) arsenophosphate (ZAP) and zirconium(IV) arsenosilicate (ZAS) were synthesized by the methods reported earlier [1, 2] which involve the precipitation of the materials, filtration through a vacuum pump, drying at a particular temperature (40—45°C), cracking in demineralized water (DMW) and then converting into the H^+-form by treatment with a dilute HNO_3 solution. Before being used for further studies, ZAP was heated at 200°C for 1 h in a muffle furnace to get a modified phase (α-ZAP) of this material which has shown improved ion-exchange behaviour and chemical stability [3]. The reported values of the Na^+ ion-exchange capacities of ZAS and α-ZAP are 1.30 and 1.03 meq/dry g, respectively.

Kinetic measurements

The materials were finely carefully ground in order to give particles of different mesh sizes (40 −60, 50 −70, 70 −100 and 100 −150). Particles of mean radii 125 μm (of ZAS) and 150 μm (of α-ZAP) were generally used in the present study unless stated otherwise. Fractions (20 ml) of the metal ion solutions were shaken with 250 mg of the exchanger (H^+-form) in several stoppered conical flasks at the desired temperatures (20, 30, 45 and 60°C) for different time intervals. The supernatant liquid was removed immediately and the determinations were done as usual by EDTA titrations [22]. Each set was repeated six times and the mean values were taken for further calculations.

Separation procedure

Two grams of the 40 −60 mesh sized particles of the exchanger (α-ZAP) in H^+-form were used for the column operation in a glass tube having an in-

ternal diameter of 0.6 cm. The column was washed thoroughly with DMW and the mixture to be separated was loaded on it, maintaining a flow rate of ca. 0.1 ml/min. The elution of the metal ion other than Cd(II) was done by 0.01 *M* HNO_3, selected on the basis of K_d values [3]. Cd(II) was removed finally with 1 *M* HNO_3. The flow rate for eluting the metal ions was kept to ca. 0.4 ml/min. Cd(II) was also quantitatively recovered from a synthetic mixture containing Mn(II), 137.5 μg; Co(II), 147.3 μg; Ni(II), 146.8 μg; Zn(II), 162.5 μg and Cd (II), 280 μg, using the same eluants as described above.

RESULTS AND DISCUSSION

A high metal ion concentration, relatively large particle size of the exchanger and vigorous shaking are the basic conditions for a particle diffusion-controlled ion-exchange phenomenon. Under these conditions the fractional attainment of equilibrium, $U(\tau)$ may be expressed as $U(\tau)$ = (the amount of exchange at time t)/(the amount of exchange at infinite time (equilibrium)).

The present system may be considered to follow the "infinite solution volume" condition [23] because $CV \gg \bar{C}\bar{V}$, where C and $\bar{C}$ are the metal-ion concentrations in the solution and exchanger phases respectively, and V and $\bar{V}$ are the volumes of these phases. The Nernst—Planck equations can be solved with some additional assumptions [24] which are valid for an inorganic ion-exchanger as the swelling changes and the specific interactions are not significant in this case. As a result, we obtain a coupled interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counterions A and B in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$, the interdiffusion coefficient assumes the value $\bar{D}_A$, A being the counter ion initially present in the ion-exchanger phase. Since in the present study the exchanger is taken in the H^+-form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

The numerical results can be expressed [25] by the explicit approximation:

$$U(\tau) = \{1 - \exp[H^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{\frac{1}{2}} \quad (1)$$

where $\tau = \bar{D}_H\, t/r_0^2$

mobility ratio, $\alpha = \bar{D}_H/\bar{D}_M$, r_0 = particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the condition $1 \leqslant \alpha \leqslant 20$ and the charge ratio, $Z_H/Z_M = 1/2$ which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed [26] as:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}} \quad (a)$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}} \quad (b)$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.14}} \qquad (c)$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained on solving Eq. (1) by the graphical method. The concentration effect on the mechanism of exchange was studied at 30°C by taking different metal ion concentrations (0.005, 0.008, 0.01, 0.025, 0.05, 0.1 and 0.12 *M*). The plots of τ vs. t (Fig. 1) at the metal ion concentrations $\geq$ 0.1 *M* for ZAS and $\geq$ 0.01 *M* for α-ZAP, are straight lines passing through the origin, thus confirming a particle diffusion-controlled exchange at these concentrations. The slopes (S) of the τ vs. t plots, as shown for the Mn^{2+}—H^+ (Fig. 2) exchange, are summarized in Table 1 for all the metal ions studied at the concentration 0.1 *M* for ZAS and 0.01 *M* for α-ZAP.

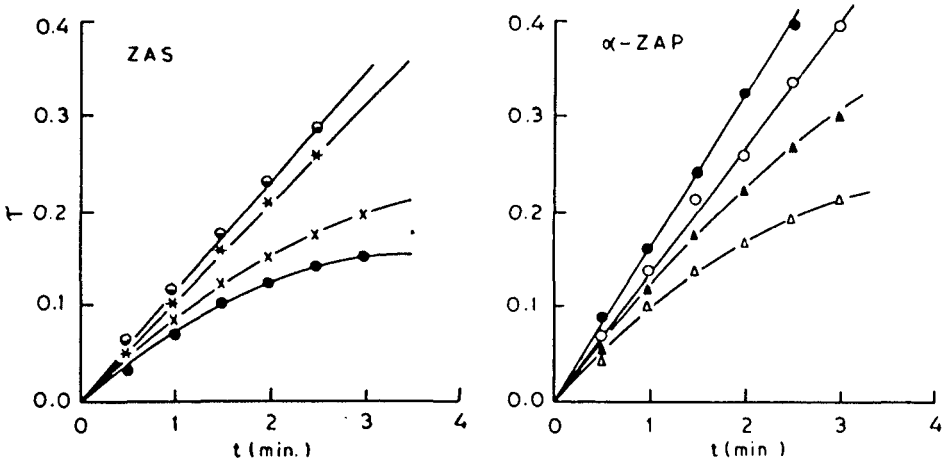


Fig. 1. Plots of τ vs. t for Mn^{2+}—H^+ exchange, using different solution concentrations at 30°C on ZAS and α-ZAP: 0.005 *M* (△); 0.008 *M* (▲); 0.01 *M* (○); 0.025 *M* (●); 0.05 *M* (×); 0.1 *M* (✱); 0.12 *M* (⊛).

The particle size has a marked effect on the rate of exchange. A plot of S vs. $1/r_0^2$ (Fig. 3) shows that the rate of exchange is inversely proportional to the particle size, a fundamental condition for a particle diffusion phenomenon.

The S values are related with $\bar{D}_H$ as follows:

$$S = \bar{D}_H/r_0^2 \qquad (2)$$

The log $\bar{D}_H$ is related linearly with $1/T$ (Figs. 4, 5) in all cases, justifying the validity of the Arrhenius equation:

$$\bar{D}_H = D_0 \exp(-E_a/RT) \qquad (3)$$

The preexponential constants (D_0) were obtained from the intercepts of these lines and the values of activation energy (E_a) were calculated from Eq. (3). The entropies of activation (ΔS^*) were obtained by substituting the D_0 val-

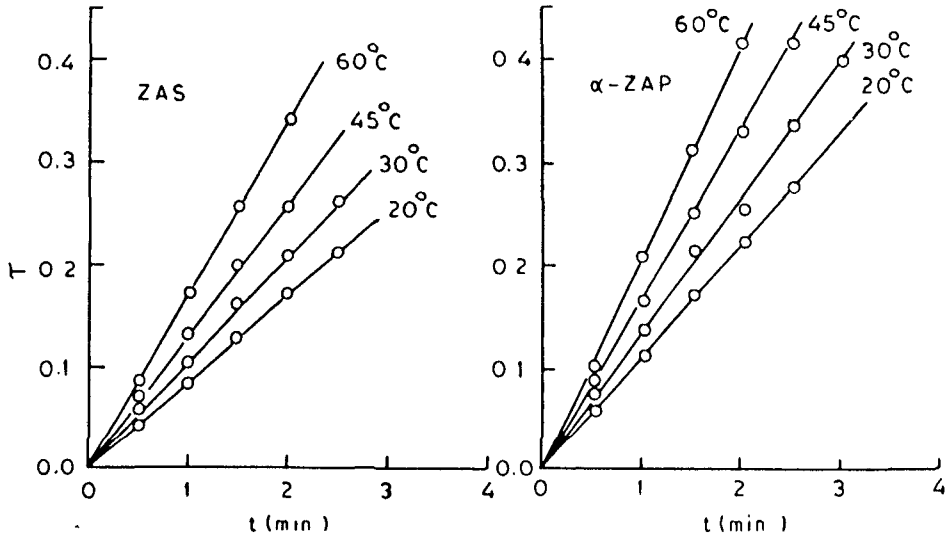


Fig. 2. Plots of τ vs. t for Mn^{2+}—H^+ exchange at different temperatures on ZAS and α-ZAP under the conditions of particle diffusion.

TABLE 1

Slopes (S) of τ vs. t plots for the transition metals on ZAS and α-ZAP

Migrating ion	S (s^{-1}) × 10^3							
	20°C		30°C		45°C		60°C	
	ZAS	α-ZAP	ZAS	α-ZAP	ZAS	α-ZAP	ZAS	α-ZAP
Mn(II)	1.43	1.83	1.73	2.22	2.17	2.78	2.86	3.45
Fe(II)	1.93	1.77	2.48	2.11	3.61	2.68	4.52	3.21
Co(II)	1.68	2.07	2.05	2.44	2.85	2.67	3.59	2.99
Ni(II)	1.84	1.94	2.16	2.21	2.83	2.72	3.44	3.19
Zn(II)	1.60	0.72	2.08	1.00	2.92	1.42	4.31	2.01
Cd(II)	1.33	1.16	1.88	1.72	2.49	2.22	3.86	3.42

ues in the equation:

$$D_0 = 2.72\, d^2\, kT/h \exp(\Delta S^*/R) \qquad (4)$$

where k and h are the Boltzmann and Planck constants, respectively; d is the ionic jump distance [27] as taken 5 Å, R (= 8.3144 J deg^{-1} mol^{-1}) is the gas constant and T is taken as 273°K. Table 2 summarizes the D_0, E_a and ΔS^* values on ZAS and α-ZAP.

As table 2 indicates, the ΔS^* values are negative on both the ion exchangers, an observation analogous to most of the materials of this class [13—16, 18—20]. It also indicates that the activation energies for the various transition metal ions studied do not have a definite trend as far as their varia-

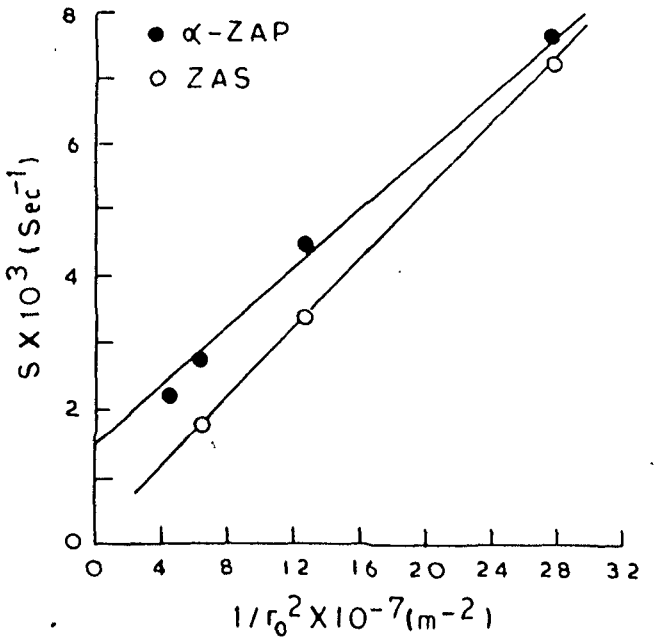


Fig. 3. Plots of S vs. $1/r_0^2$ for Mn^{2+} at 30°C on ZAS and α-ZAP.

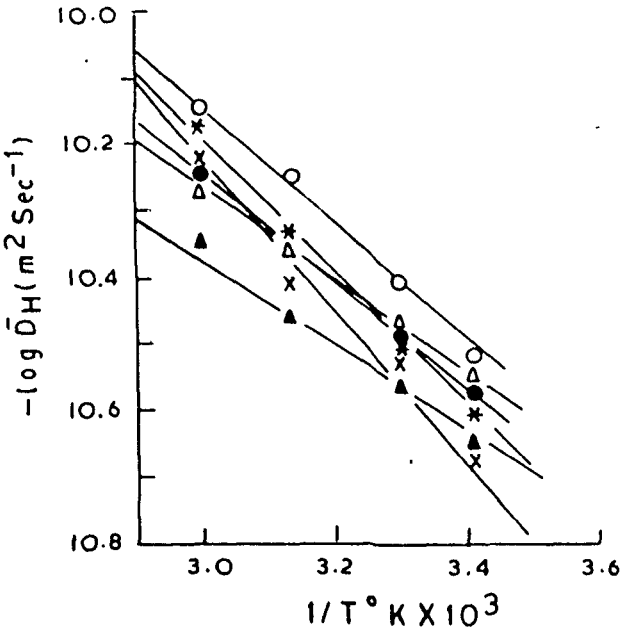


Fig. 4. Plots of $-\log \bar{D}_H$ vs. $1/T°K$ for Fe^{2+} (○); Co^{2+} (●); Ni^{2+} (△); Mn^{2+} (▲); Zn^{2+} (*) and Cd^{2+} (×) on ZAS.

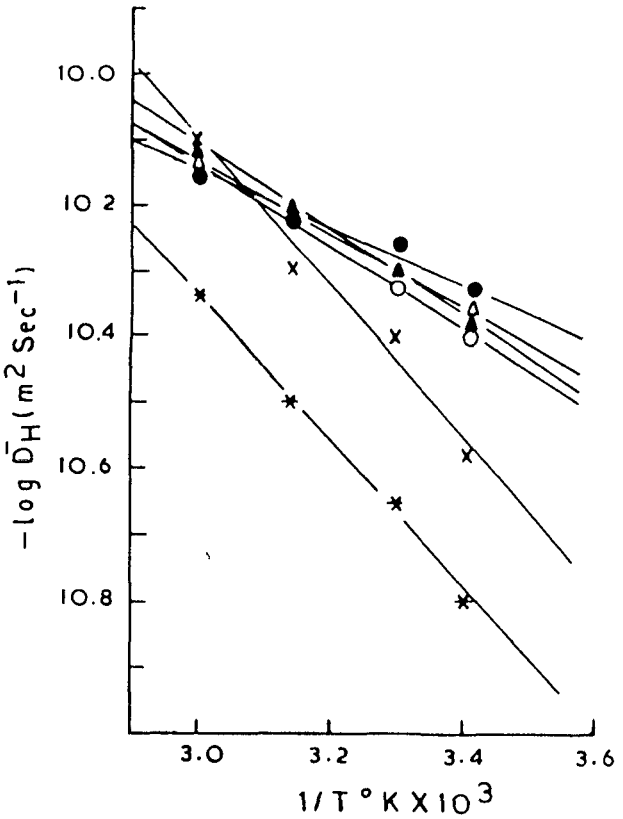


Fig. 5. Plots of $-\log \bar{D}_H$ vs. $1/T^\circ K$ for Fe^{2+} (○); Co^{2+} (●); Ni(II) (△); Mn(II) (▲); Zn(II) (*) and Cd(II) (×) on α-ZAP.

TABLE 2

D_0, E_a and ΔS^* values for the H^+-exchange with transition metal ions on ZAS and α-ZAP

Metal ion exchanging with H^+	Ionic radius (A*)	D_0 ($m^2 s^{-1}$)		E_a (kJ $mole^{-1}$)		S^* (J deg^{-1} mol^{-1})	
		ZAS	α-ZAP	ZAS	α-ZAP	ZAS	α-ZAP
Mn(II)	0.91	3.55×10^{-8}	7.08×10^{-9}	12.26	12.50	−58.15	−52.40
Fe(II)	0.83	2.95×10^{-8}	5.62×10^{-9}	16.62	12.02	−40.53	−54.32
Co(II)	0.82	1.74×10^{-8}	1.51×10^{-9}	15.78	8.482	−44.94	−65.23
Ni(II)	0.78	7.76×10^{-8}	3.54×10^{-9}	13.69	10.74	−51.64	−58.15
Zn(II)	0.83	7.41×10^{-8}	8.71×10^{-8}	19.52	20.96	−32.88	−33.49
Cd(II)	1.03	2.04×10^{-7}	2.09×10^{-7}	22.42	21.74	−24.45	−24.26

tion with the ionic radii is concerned. It is in contrast to the observation made earlier [7, 8] on these materials for the alkaline earths. It may be due to a more distinct variation in the ionic radii in a particular group than in a

period. The activation energy is maximum for Cd(II) on both the exchangers. However, the variation in its value for the different metal ions is much wider on α-ZAP as compared to the one on ZAS. These observations are supplemented by the achieved separations of Cd(II) from Co(II), Ni(II), Mn(II) and Zn(II) on α-ZAP columns as shown in Fig. 6. The achievement of the Cd(II)—Zn(II) separation appears to be unusual on the basis of our kinetic observations. They are separated although their E_a values are similar, which depend upon the mobility ratios ($\bar{D}_H/\bar{D}_M$). However, the separation tenden-

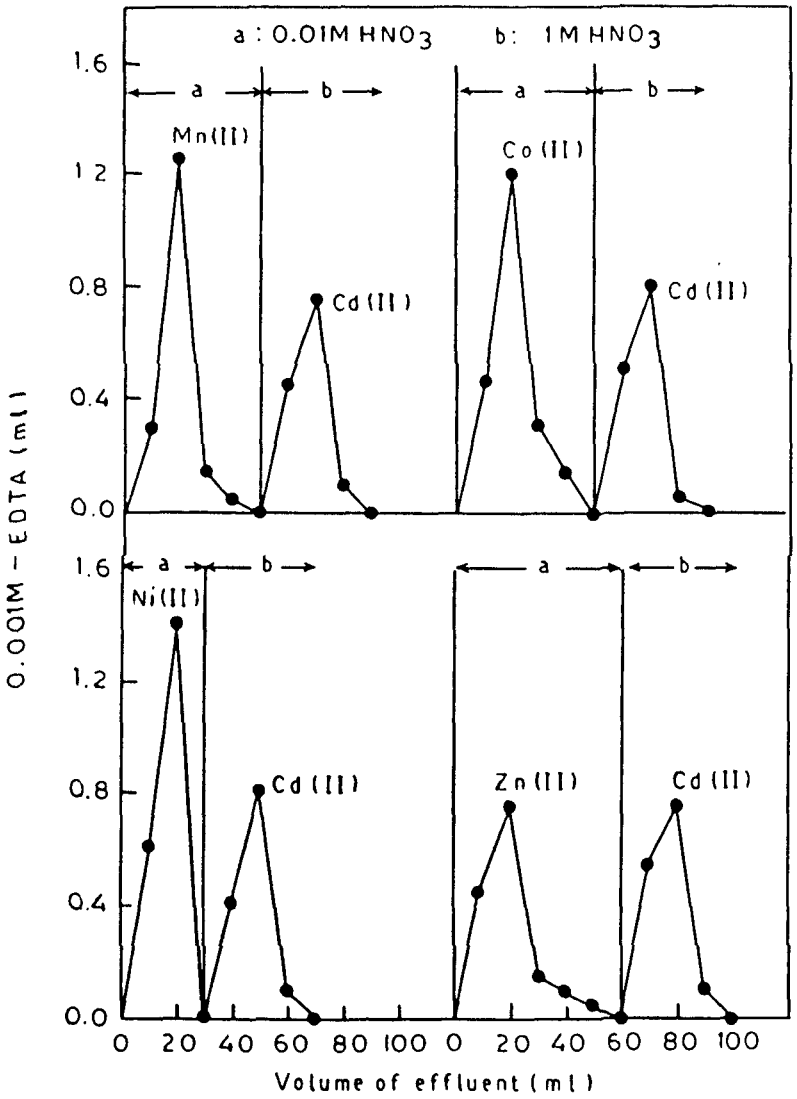


Fig. 6. Elution curves for the separation of Cd(II) from other metal ions on α-ZAP columns.

cy of the two metals depends on their ionic sizes also, which are very different in this case. This may be the reason for the unusual behaviour of the material (α-ZAP) for this particular separation. Thus, these studies, based on the Nernst–Planck equations, give a more appropriate explanation for the separation mechanism on inorganic ion-exchangers as compared to the old Bt criterion because of the introduction of the term "mobility" in the new approach.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Mohsin Qureshi for research facilities. The financial assistance provided by the C.S.I.R., India, is gratefully acknowledged.

REFERENCES

1 K.G. Varshney and A. Premadas, Sep. Sci. Technol., 16 (1981) 793.
2 K.G. Varshney, S. Agrawal and K. Varshney, Sep. Sci. Technol., 18 (1983) 59.
3 K.G. Varshney, K. Varshney and S. Agrawal, Sep. Sci. Technol., (in press).
4 K.G. Varshney, S. Agrawal, K. Varshney, A. Premadas, M.S. Rathi and P.P. Khanna, Talanta, (in press).
5 K.G. Varshney, S. Agrawal and K. Varshney, J. Liquid Chromatogr., (in press).
6 K.G. Varshney, S. Agrawal and K. Varshney, Anal. Lett., 16 (1983) 685.
7 K.G. Varshney, S. Agrawal and K. Varshney, Acta Chim., (in press).
8 K.G. Varshney, S. Agrawal and K. Varshney, Submitted to Colloid Polym. Sci.
9 K.G. Varshney and S. Rani, Ind. J. Chem., (in press).
10 K.G. Varshney and U. Sharma, Acta Chim., (in press).
11 W.Z. Nernst, Phys.-Chem., 2 (1888) 613 and 4 (1889) 729.
12 M. Planck, Ann. Phys. Chem., 39 (1890) 161.
13 J.P. Rawat and P.S. Thind, J. Phys. Chem., 80 (1976) 1384.
14 A. Dyer and J.S. Gill, J. Inorg. Nucl. Chem., 39 (1977) 665.
15 K. Bunzl, J. Inorg. Nucl. Chem., 39 (1977) 1049.
16 J.P. Rawat and D.K. Singh, J. Inorg. Nucl. Chem., 40 (1978) 897.
17 I.P. Saraswat, S.K. Srivastava and A.K. Sharma, Can. J. Chem., 57 (1979) 1214.
18 J.P. Rawat and M.A. Khan, J. Inorg. Nucl. Chem., 42 (1980) 905.
19 N.J. Singh, J. Mathew and S.N. Tandon, J. Phys. Chem., 84 (1980) 21.
20 K.G. Varshney and A. Premadas, Ind. J. Chem., 20 (1981) 841.
21 F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, p. 266.
22 C.N. Reilley, R.W. Schmid and Fawzys, J. Chem. Educ., 36 (1959) 555.
23 Ref. 21, p. 260.
24 Ref. 21, p. 268.
25 Ref. 21, p. 270.
26 Ref. 21, p. 271.
27 R.M. Barrer, H.F. Bartholomew and L.V.C. Rees, J. Phys. Chem. Solids, 12 (1961) 21.

Acta Chimica Hungarica 116 (1), pp. 69—75 (1984)

3.9 ION EXCHANGE KINETICS OF ALKALINE EARTHS ON Zr(IV) ARSENOSILICATE CATION EXCHANGER

ACTIVATION ENERGY AS A LINEAR FUNCTION OF THE IONIC MOBILITIES AND RADII

K. G. VARSHNEY*, S. AGRAWAL and K. VARSHNEY

(Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh-202001, India)

Received May 17, 1983

Accepted for publication June 28, 1983

A new approach based on the Nernst–Planck equations has been applied to study the ion exchange kinetics for the exchange reactions of Mg(II), Ca(II), Sr(II) and Ba(II) with H^+-ions at various temperatures on the zirconium(IV) arsenosilicate phase. Under the conditions of particle diffusion, the rate of exchange was found to be independent of the metal ion concentration at and above 0.1 *M* in aqueous medium. Energy and entropy of activation were determined and found to vary linearly with the ionic radii and mobilities of alkaline earths, a unique feature observed for an inorganic ion exchanger. The results are useful for predicting the ion exchange processes occurring on the surface of an inorganic material of the type studied.

Introduction

Inorganic ion exchangers are useful for the separation of metals [1,2]. Although a large number of such materials have been prepared, only a few of them have been reported for their kinetic studies [3—21]. Moreover, the earlier approaches are based on the old '*Bt* criterion' [22] which is useful only for ions having similar effective diffusion coefficients i.e. for the isotope exchange processes. In an ion exchange phenomenon, however, the fluxes of two different ionic species are coupled into one another [23], and, therefore, a single diffusion coefficient can not describe the actual process. This article, therefore, summarizes our efforts to apply the Nernst—Planck equations [24, 25] which take into account the exchange of ions having different mobilities to determine the various kinetic parameters. Zirconium(IV) arsenosilicate (ZAS) has been selected because of its fairly good stability, reproducibility and applicability in the analysis of some real samples [26, 27].

* To whom correspondence should be addressed

Experimental

Reagents and chemicals

Zirconyl chloride and arsenic acid used in this study were BDH (England) products while sodium silicate was the product of Riedel (DEHAENAG, Seelze Hannover). Other reagents and chemicals were of analaR grade.

Apparatus

A water-bath incubator shaker having a temperature variation of ± 0.5 °C was used in the equilibrium studies.

Synthesis of the ion exchange material

ZAS was prepared as earlier [26] by the following method: An aqueous (0.1 *M*) sodium silicate solution, made acidic (pH 0—1) by adding HCl, was mixed with an aqueous (0.1 *M*) zirconyl chloride solution and the pH of the mixture was raised to 8—10 by a slow addition of ammonium hydroxide with intermittent shaking to obtain a slurry. After filtration and washing with demineralized water (DMW), it was treated with a 1 : 1 (*V*/*V*) mixture of 0.5 *M* solutions of arsenic and nitric acids. This resulted in a gel which was digested at room temperature for 24 h and then separated by filtration. It was washed thoroughly to remove excess acid, dried at 45 °C and cracked into small granules by putting in DMW and then converted into the H^+-form using 1 *M* HNO_3. They were finally washed with DMW and dried as usual for further study. The Na^+-exchange capacity of the material was found to be 1.3 meq/dry g as determined by the column process.

Kinetic measurements

Ion exchange particles of mean radii 250 μm (55—65 mesh size) were used in this experiment. 20 mL fractions of the 0.1 *M* metal ion solution (Mg, Ca, Sr and Ba) were shaken with 200 mg of the exchanger in several stoppered conical flasks at the desired temperature (20, 30, 45 and 60 °C, ± 0.5 °C) for different time intervals. Supernatant liquid was immediately removed by filtering it through a Whatman No. 4 filter paper. Determinations were done by EDTA titrations [28] using Eriochrome Black T as an indicator. Each run was repeated at least six times.

Results and Discussion

A study of the concentration effect on the rate of exchange for Mg^{2+}—H^+ exchange at 30 °C shows that at concentrations <0.1 *M* the initial rate of exchange is proportional to [Mg(II)]. At concentrations ≥ 0.1 *M* it is found to be independent of the metal ion concentration. Under the conditions of particle diffusion control, a relatively large particle size of the exchanger and vigorous shaking, the fractional attainment of equilibrium may be given as

$$U(\tau) = \frac{\text{the amount of exchange at time } t}{\text{the amount of exchange at infinite time}}$$

A plot of $U(\tau)$ versus t (Fig. 1) indicates that the fractional attainment of equilibrium is faster at a higher temperature, an observation analogous to the other materials of this class. Although, this is a limited bath system, the equation applicable to an infinite bath can be used here because $CV \gg \bar{C}\bar{V}$ where C and $\bar{C}$ are the metal ion concentrations in the solution and the exchanger

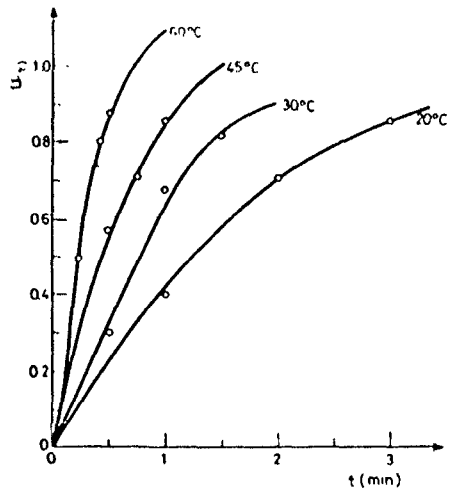


Fig. 1. Plot of $U(\tau)$ versus t for $Mg^{2+}-H^+$ exchange at different temperatures on ZAS

phases, respectively, while V and $\bar{V}$ are the volumes of these phases. The Nernst—Planck equations can be solved with some additional assumptions [23] which are valid for inorganic ion exchangers as the swelling changes and the specific interactions are not significant in this case. As a result we obtain a coupled interdiffusion coefficient $\bar{D}_{AB}$, the value of which depends on the relative concentrations of the counter ions 'A' and 'B' in the exchanger phase ($\bar{C}_A$ and $\bar{C}_B$). For $\bar{C}_A \ll \bar{C}_B$, the interdiffusion coefficient assumes the value $\bar{D}_A$, 'A' being the counter ion initially present in the ion exchanger phase. Since in the present study the exchanger is taken in the H^+ form, $\bar{D}_A$ may be replaced by $\bar{D}_H$.

Thus, on the basis of the Nernst—Planck equations the numerical results can be expressed by the explicit approximation [25]

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\,\tau + f_2(\alpha)\,\tau^2 + f_3(\alpha)\,\tau^3)]\}^{\frac{1}{2}} \qquad (1)$$

where $\tau \equiv \dfrac{\bar{D}_H t}{r_0^2}$,

mobility ratio, $\alpha \equiv \dfrac{\bar{D}_H}{\bar{D}_M}$, r_0 = particle radius and $\bar{D}_M$ is the interdiffusion coefficient of the metal ion. Under the conditions $1 \leq \alpha \leq 20$ and $\dfrac{Z_H}{Z_M} = \dfrac{1}{2}$ which are fulfilled in the present case, the three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ can be expressed as

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}}$$

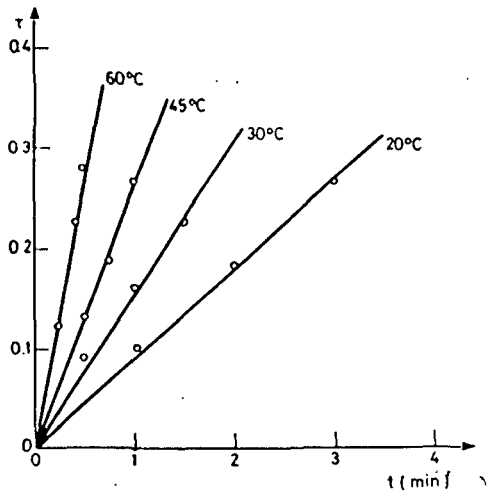


Fig. 2. Plot of τ versus t for Mg^{2+} — H^+ exchange at different temperatures on ZAS

$$f_2(\alpha) = -\frac{1}{0.96 \cdot 2.0\,\alpha^{0.4635}}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\,\alpha^{1.14}}$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained by solving the equation (1) by graphical method. Plots of τ vs. t at the four different temperatures (Fig. 2) for Mg(II) ion are shown at a concentration 0.1 M which are straight lines passing through the origin. This confirms that the phenomenon is particle-diffusion controlled. Table I Slopes (S) of such lines for all the four alkaline earths are given in Table I which are related with $\bar{D}_H$ as follows;

$$S = \frac{\bar{D}_H}{r_0^2} \tag{2}$$

Table I

Slopes (S) of the various τ versus time plots for alkaline earths on ZAS

Migrating ion	S (s^{-1})			
	20 °C	30 °C	45 °C	60 °C
Mg(II)	1.50×10^{-3}	2.56×10^{-3}	4.42×10^{-3}	9.26×10^{-3}
Ca(II)	1.75×10^{-3}	2.78×10^{-3}	4.90×10^{-3}	11.10×10^{-3}
Sr(II)	1.34×10^{-3}	2.08×10^{-3}	4.35×10^{-3}	7.90×10^{-3}
Ba(II)	1.08×10^{-3}	1.79×10^{-3}	3.55×10^{-3}	7.20×10^{-3}

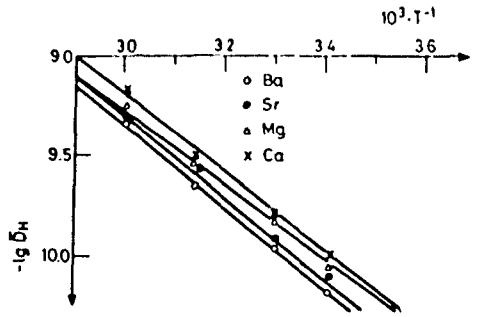


Fig. 3. $\log \bar{D}_H$ against T^{-1}

The values of $\log \bar{D}_H$ obtained by this equation were plotted against $1/T$. Straight lines are obtained for all the metal ions studied, as shown in Fig. 3. justifying the validity of the Arrhenius equation;

$$\bar{D}_H = D_0 \exp(-E_a/RT) \tag{3}$$

The pre-exponential constants D_0 are obtained from the intercepts of the lines and then the E_a values can be calculated by the use of this equation.

The entropy of activation (ΔS^*) is obtained by substituting D_0 into the following equation

$$D_0 = 2.72\, d^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \tag{4}$$

where k and h are the Boltzmann and Planck's constants, d is the ionic jump distance taken [29] as 0.5 nm, R is the gas constant and T is taken as 273 °K. The values of D_0, E_a and ΔS^* are summarized in Table II. As the results show E_a increases with the ionic radii as usual. Positive entropy changes may be due to the deformation in the shape of the matrix because of the introduction

Table II

D_0, energy of activation and entropy of activation of alkaline earths on ZAS in H^+-form

Migrating ion	Ionic mobility	Ionic radii	Hydrated ionic radii	D_0	E_a	ΔS^*
	$m^2 \cdot V^{-1} \cdot s^{-1} \cdot 10^8$	nm	nm	$m^2 \cdot s^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
Mg(II)	5.5	0.078	0.310	1.36×10^{-4}	34.53	29.57
Ca(II)	6.2	0.106	0.200	2.93×10^{-4}	36.05	35.98
Sr(II)	6.2	0.127	0.180	3.85×10^{-4}	37.55	38.25
Ba(II)	6.6	0.143	0.150	4.47×10^{-4}	38.28	39.49

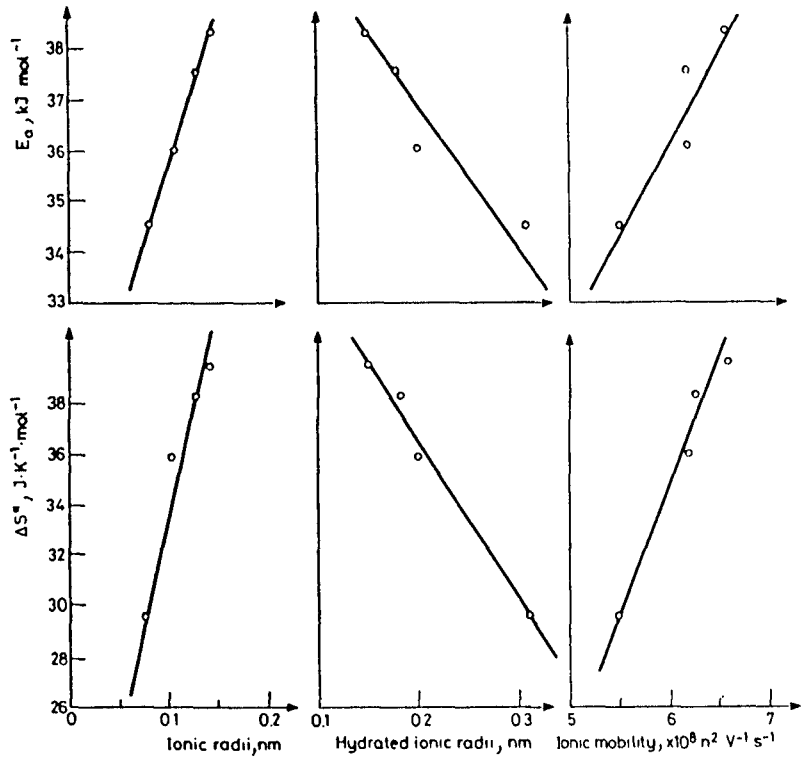


Fig. 4. Variation of E_a and ΔS^* with ionic radii, hydrated ionic radii and ionic mobilities of the alkaline earths on ZAS

of larger ions in place of the previously present H^+ ions in the matrix. A similar behaviour has also been observed earlier for the exchange of Co(III) amine complex cations on chromium ferrocyanide gel [17]. We found linear relations between E_a and ΔS^* values and the ion mobilities and radii of the alkaline earths as shown in Fig. 4.

The authors are thankful to Prof. Mohsin Qureshi for research facilities and to the CSIR (India) for financial assistance.

REFERENCES

[1] Nachod, F. C., Schubert, J.: Ion Exchange Technology, p. 287, Academic Press Inc. Publishers, New York 1956
[2] Clearfield, A., Nancollas, G. H., Blessing, R. H.: in Ion Exchange and Solvent Extraction, Vol. 5 (Eds J. A. Marinsky and Y. Marcus), Marcel Dekker, New York 1973
[3] Nancollas, G. H., Paterson, R.: J. Inorg. Nucl. Chem., **22**, 259 (1961)
[4] Harvie, S. J., Nancollas, G. H.: J. Inorg. Nucl. Chem., **30**, 273 (1968)
[5] Ruvarac, A. L., Vesely, V.: J. Inorg. Nucl. Chem., **32**, 3939 (1970)
[6] Clearfield, A., Medina, A. S.: J. Inorg. Nucl. Chem., **32**, 2775 (1970)
[7] Dyer, A., Ocon, F. T.: J. Inorg. Nucl. Chem., **33**, 3153 (1971)
[8] Ruvarac, A. L.: J. Chromatogr., **60**, 235 (1971)

[9] Choudhury, D., Mukherjee, S. K.: J. Inorg. Nucl. Chem., **33**, 1933 (1971)
[10] Ruvarac, A. L., Trtanj, M. I.: J. Inorg. Nucl. Chem., **34**, 3893 (1972)
[11] Alberti, G., Bertrami, R., Cascoila, M., Costantino, U., Gupta, J. P.: J. Inorg. Nucl. Chem., **38**, 843 (1976)
[12] Rawat, J. P., Thind, P. S.: J. Phys. Chem., **80**, 1384 (1976)
[13] Herman, R. G., Clearfield, A.: J. Inorg. Nucl. Chem., **38**, 853 (1976)
[14] Dyer, A., Gill, J. S.: J. Inorg. Nucl. Chem., **39**, 665 (1977)
[15] Bunzl, K.: J. Inorg. Nucl. Chem., **39**, 1019 (1977)
[16] Rawat, J. P., Singh, D. K.: J. Inorg. Nucl. Chem., **40**, 897 (1978)
[17] Saraswat, I. P., Srivastava, S. K., Sharma, A. K.: Can. J. Chem., **57**, 1214 (1979)
[18] Rawat, J. P., Khan, M. A.: J. Inorg. Nucl. Chem., **42**, 905 (1980)
[19] Singh, N. J., Mathew, J., Tandon, S. N.: J. Phys. Chem., **84**, 21 (1980)
[20] Singh, N. J., Tandon, S. N.: Ind. J. Chem., **19A**, 416 (1980)
[21] Varshney, K. G., Premadas, A.: Ind. J. Chem., **20A**, 841 (1981)
[22] Boyd, G. E., Adamson, A. W., Myers, L. S.: J. Am. Chem. Soc., **69**, 2836 (1947)
[23] Helfferich, F.: Ion Exchange, Ch. 6, Mc Graw-Hill, New York 1962
[24] Nernst, W. Z.: J. physik. Chem., **2**, 613 (1888); **4**, 129 (1889)
[25] Planck, M.: Ann. Phys. Chem., **39**, 161 (1890)
[26] Varshney, K. G., Agrawal, S., Varshney, K.: Sep. Sci. Technol., **18**, 59 (11983)
[27] Varshney, K. G., Agrawal, S., Varshney, K.: J. Liq. Chromatogr., **6**, 1535 (1983)
[28] Reilley, C. N., Schmid, R. W., Fawzys: J. Chem. Educ., **36**, 555 (1959)
[29] Barrer, R. M., Bartholomew, R. F., Rees, L. V. C.: J. Phys. Chem. Solids, **12**, 21 (1961)

Indian Journal of Chemistry
Vol. 23A, February 1984, pp. 152-154

3.10 Kinetics of Exchange of Some Divalent Metal Ions on Phosphosilicates of Zirconium(IV) & Thorium(IV) & Arsenosilicate of Tin(IV)

K G VARSHNEY*, UMA SHARMA, S ANWAR & A A KHAN

Chemistry Section, Faculty of Engg & Tech., Aligarh Muslim University, Aligarh 202001

Received 21 *March* 1983; *revised* 30 *September* 1983; *accepted* 17 *October* 1983

Kinetics of the exchange reactions of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions on Zr(IV) and Th(IV) phosphosilicates and Sn(IV) arsenosilicate cation exchangers have been studied at 25°, 32°, 50° and 65°C under the conditions favourable to the particle diffusion mechanism only. The rate of exchange has been found to be independent of metal ion concentration at and above 0.01 mol dm^{-3} in aqueous medium. Various kinetic parameters such as self-diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation ($\Delta S^{\ddagger}$) have been calculated.

In continuation of earlier work from our laboratory on the kinetics of exchange of some divalent ions on tin(IV) arsenophosphate[1], antimony(V) silicate[2] and zirconium(IV) arsenosilicate[3], we present herein the results of kinetics of exchange of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} ions on zirconium(IV), thorium(IV) and tin(IV) cation exchangers.

Zirconyl chloride, thorium nitrate (both BDH), stannic chloride (P.p.H. Polskie Odezynniki Chemiczire Gliwica) and sodium silicate (Reidel) were used as such. All other reagents and chemicals were of AR grade.

Zr(IV) and Th(IV) phosphosilicates (abbreviated as ZPS and TPS respectively) were prepared as follows: To an aq. solution of sodium silicate (1000 ml, 0.1 mol dm^{-3}) were added conc. HCl (50 ml) and aq. zirconium oxychloride solution (1000 ml, 0.1 mol dm^{-3}). The *p*H of the mixture was kept at 9-10 by adding NH_4OH, the resultant slurry was allowed to stand overnight, filtered, washed with demineralised water (DMW) and mixed with H_3PO_4-HNO_3 mixture (total 1000 ml, 1 mol dm^{-3} each). The gel thus obtained was kept overnight, filtered, washed thoroughly with DMW, dried at 45°C in an air oven and put in DMW to form small granules, which were converted into the H^+ form by treating them with 1 mol dm^{-3} HNO_3. Thorium(IV) phosphosilicate (TPS) was prepared in a similar manner by taking thorium nitrate, $Th(NO_3)_4.6H_2O$ instead of $ZrOCl_2.8H_2O$. The Na-ion exchange capacities of the cation exchangers ZPS and TPS were found to be 2.19 and 1.66 meq/dry g, respectively.

Sn(IV) arsenosilicate (SAS) was prepared as follows: Decimolar solutions of sodium silicate, sodium arsenate and stannic chloride were mixed in 1:1:1 (v/v) ratio and the *p*H of the gel adjusted at 1 with HNO_3. It was kept at room temperature for 24 hr, filtered, washed with DMW several times to remove excess reagents, dried at 45°C in an air oven and placed in DMW to form small granules which were converted into the H^+-form by treating with HNO_3 (1 mol dm^{-3}) as usual. The Na-ion exchange capacity for the dried material was found to be 0.95 meq/dry g.

For kinetic measurements aliquots of the metal ion solutions (20 ml) were shaken for different periods with the various mesh-sized particles (25-50, 50-70, 70-100 and 100-150) of the cation exchangers (0.2 g) in a temperature-controlled (±0.5°) shaker at different temperatures (25°, 32°, 50° and 65°C). The supernatant liquids were then removed for the metal ion determinations. To study the concentration effect the metal solutions of varying concentrations (0.005, 0.008, 0.01, 0.05 and 0.1 mol dm^{-3}) were used with the cation exchanger of a definite particle size (average particle radius ~125 μm).

A study of the concentration effect on the rate of exchange at 32°C shows that for the Mg^{2+}-H^+ and Mn^{2+}-H^+ exchanges the initial rate of exchange is proportional to the [metal ion] below 0.01 mol dm^{-3} indicating exchange by film diffusion. Above 0.01 mol dm^{-3}, however, the rate of exchange is independent of the [metal ion] indicating that exchange occurs predominantly by particle-diffusion. In this respect the behaviour of exchangers (ZPS, TPS and SAS) is similar to that of other cation exchangers studied earlier[2,3].

Although this is a limited bath system, the equation applicable to an infinite bath can be used here because $CV \gg \bar{C}\bar{V}$, where C and $\bar{C}$ are the metal ion concentrations in the solution and exchanger phases respectively and V and $\bar{V}$ are the volumes of these two phases. Hence, the Nernst-Planck equations can be solved with some additional assumptions[4], which are valid for inorganic ion-exchangers as the swelling changes and the specific interactions are not significant in this case. On the basis of this treatment:

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3]\}^{\frac{1}{2}} \quad \ldots (1)$$

where $\tau = \bar{D}_{\mathrm{H}}\, t/r_0^2$, and the mobility ratio $\alpha = \bar{D}_{\mathrm{H}}/\bar{D}_{\mathrm{M}}$, r_0 = particle radius and $\bar{D}_{\mathrm{M}}$ is the inter-diffusion coefficient of the metal ion. Under the conditions $1 \leqslant \alpha$

Table 1—Slope of Various τ Versus Time Plots as a Function of Temperature and Particle Size of Alkaline Earths and Transition Metals on Zirconium Phosphosilicate

Migrating Ion	Particle radius (μm)	$10^4 \times$ slopes (s^{-1}) at 25	32	50	65 C
Mg^{2+}	225		3 90		
			(1 17)		
			(4 00)		
	125	3 33	4 44	5 56	6 67
		(1.00)	(1 53)	(2 00)	(2 67)
		[4.00]	[5 17]	[6 00]	[9.00]
	78.6		5 00		
			(2.00)		
			[6 67]		
	62.5		5 50		
			(2.17)		
			[8 00]		
Ca^{2+}	125	5.56	6.67	12 12	13 88
		(1.67)	(2 33)	(2 67)	(3 67)
		[0 83]	[2 33]	[3 00]	[4 33]
Ba^{2+}	125	3.33	6 67	8 89	16 66
		(1.33)	(1.67)	(2 33)	(2 83)
		[2.67]	[4.33]	[5 67]	[8 00]
Sr^{2+}	125	5 00	7 78	8 89	11.66
		(1.83)	(2 33)	(3.17)	(3 67)
		[1.67]	[2 50]	[3 00]	[4 00]
Mn^{2+}	225		0 78		
			(1 83)		
			[31.11]		
	125	1 22	1.56	1 78	2 44
		(1.83)	(3.17)	(4.17)	(5 33)
		[25.60]	[42 50]	[68 90]	[91 10]
Fe^{2+}	125	6.67	7 78	11.11	14 44
		(1.00)	(1 33)	(2 17)	(2 67)
		[6.70]	[13 30]	[33 30]	[44 40]
Co^{2+}	125	0 88	1.22	1 78	3 00
		(1.00)	(1.50)	(2 83)	(4 83)
		[54 40]	[88 90]	[113 30]	[122 20]
Ni^{2+}	125	1.11	1 33	1 78	3 33
		(1 67)	(2 33)	(3.17)	(4 00)
		[7 80]	[17 80]	[31.10]	[40 00]

Values in circular brackets are for TPS and values in square brackets are for SAS.

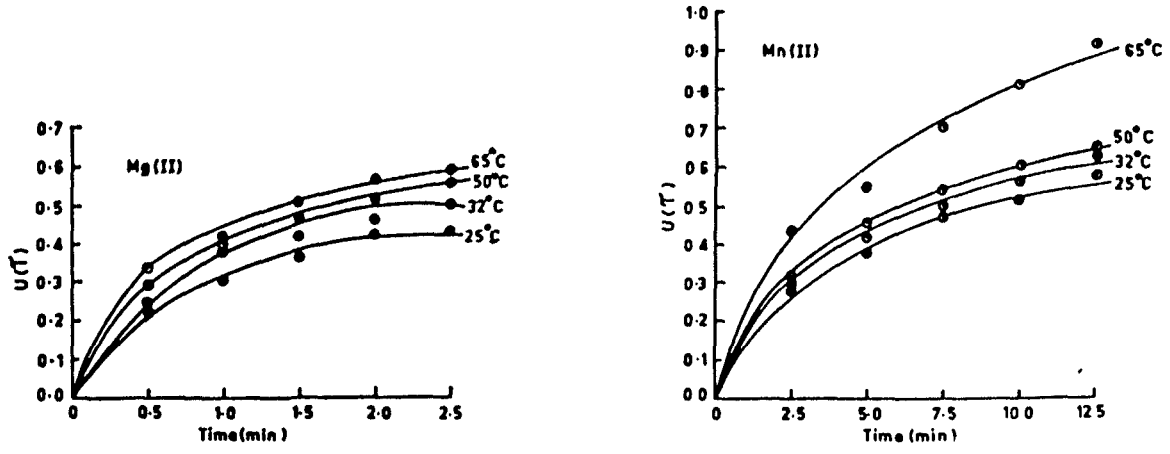


Fig. 1—Plot of fractional attainment of equilibrium against time for Mg(II) and Mn(II) ions on ZPS

Table 2—Self-diffusion Coefficient (D_0) Energy of Activation (E_a) and Entropy of Activation ($\Delta S\ddagger$) of Alkaline Earths and Transition Metals on Zirconium Phosphosilicate

Migrating ion	10^9 Ionic mobility ($m^2 V t^{-1} s^{-1}$)	10^2 Ionic radii (nm)	D_0 ($m^2 s^{-1}$)	E_a (kJ mol^{-1})	$-\Delta S\ddagger$ (JK^{-1}mol^{-1})
Mg^{2+}	55	7 80	$1\ 9\times10^{-9}$	14 53	63 32
			($1\ 26\times10^{-9}$)	(16 20)	(66 76)
			[$2\ 51\times10^{-8}$]	[20 07]	[41 88]
Ca^{2+}	62	10 60	$1\ 91\times10^{-8}$	10 02	44.17
			($2\ 00\times10^{-9}$)	(16 41)	(62 93)
			[$2\ 00\times10^{-7}$]	[28 54]	[24 65]
Ba^{2+}	66	14 30	$1\ 82\times10^{-6}$	31 46	6 27
			($5\ 25\times10^{-9}$)	(18 71)	(54 89)
			[$1\ 82\times10^{-7}$]	[31 46]	[6 27]
Sr^{2+}	62	12 70	$5\ 25\times10^{-8}$	20 90	35 75
			($2\ 63\times10^{-8}$)	(22 05)	(41 49)
			[$1\ 66\times10^{-7}$]	[26 86]	[26 18]
Mn^{2+}	55	9 10	$1\ 15\times10^{-9}$	15 78	67 53
			($4\ 37\times10^{-9}$)	(17 56)	(56 43)
			[$1\ 82\times10^{-7}$]	[20 17]	[25 41]
Fe^{2+}	54	6 70	$1\ 10\times10^{-7}$	26 92	29 62
			($6\ 03\times10^{-9}$)	(20 33)	(53 75)
			[$4\ 79\times10^{-5}$]	[49 34]	[−59 20]
Co^{2+}	55	8 20	$2\ 88\times10^{-8}$	24 56	40 73
			($7\ 94\times10^{-7}$)	(32 40)	(13 16)
			[$7\ 24\times10^{-8}$]	[16 31]	[33 07]
Ni^{2+}	52	7 80	$4\ 37\times10^{-8}$	25 50	37 28
			($6\ 31\times10^{-9}$)	(19 02)	(53 36)
			[$7\ 59\times10^{-6}$]	[31 98]	[−5 60]

Values in circular brackets are for TPS and values in square brackets are for SAS

$\leqslant 20$ and the charge ratio $Z_H/Z_M = 1/2$, the τ values were calculated.

A study of the effect of particle size and temperature on the rate of exchange shows that at [metal ion] $= 0.01$ mol dm^{-1} the τ versus time plots are all linear passing through the origin at all temperatures studied. Also, the slope (Table 1) increases with increase in the particle size which is a fundamental condition for a particle controlled process.

The effect of temperature on the fractional attainment of equilibrium, $U(\tau)$ which is the ratio of the total amount exchanged at time t and that at infinite time is illustrated in Fig. 1. It shows that the equilibrium is attained faster at a higher temperature, an observation analogous to other cation exchangers of this class.

The plots of $-\log \bar{D}_{11}$ versus 1/T are linear and the values of D_0, E_a and $\Delta S\ddagger$ calculated from the plots are summarized in Table 2 A comparison of the results reveals that while for TPS the E_a values are almost the same for all the four alkaline earths, they are widely different for ZPS and SAS. The energy of activation is maximum for Ba^{2+} for exchange on ZPS and SAS indicating greater affinity of these exchangers for this metal ion. It is supported by the fact that separation of Ba^{2+} from Mg^{2+}, Ca^{2+} and Sr^{2+} has conveniently been achieved on SAS[5] and ZPS[6] columns. The entropy of activation ($\Delta S\ddagger$) is related to the ionic radii to some extent on SAS for the alkaline earths. For the transition metal ions studied a slightly different behaviour is observed on SAS As expected, the entropy change is negative for the Mn^{2+}-H^+ and Co^{2+}-H^+ exchanges However, the $\Delta S\ddagger$ change is positive, for the Fe^{2+}-H^+ and Ni^{2+}-H^+ exchanges, probably due to the deformation of the shape of the matrix as a result of exchange processes[7]

The authors are thankful to Prof. Mohsin Qureshi for research facilities and to the CSIR (New Delhi) for the financial assistance to US and SA

References

1 Varshney K G & Permadas A, *Indian J Chem* 20A (1981) 841
2 Varshney K G & Rani S, *Indian J Chem*, 22A (1983) 657
3 Varshney K G, Agrawal S & Varshney K, *Acta Chimica* (In press)
4 Helfferich F, *Ion exchange* (Mc Graw-Hill, New York) 1962, p 268
5 Varshney K G Khan A A, Maheshwari A, Anwar S & Sharma U, *Indian J Technol* (In Press)
6 Ramaswamy R M S, Jangida B L, Sundaresan M, *Proc Ion Exch Symp*, (1978) 187
7 Saraswat I P, Srivastava S K & Sharma A K, *Can J Chem*, 57 (1979) 1214

Colloids and Surfaces, 18 (1986) 67—73
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

3.11

EVALUATION OF THE DIMENSIONLESS TIME PARAMETER FOR SOME PARTICLE DIFFUSION CONTROLLED FORWARD AND REVERSE H(I)—METAL(II) EXCHANGES

K.G. VARSHNEY, KANAK VARSHNEY and SANJAY AGRAWAL

Analytical Laboratories, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001 (India)

(Received 31 October 1984; accepted in final form 18 December 1985)

ABSTRACT

The dimensionless time parameter (τ) has been evaluated as a function of fractional exchange of H(I) for some bivalent ions and of the bivalent ions for H(I) using the explicit approximation given by Helfferich et al., applicable to a particle diffusion-controlled ion-exchange process. The calculations have been made using a computer.

INTRODUCTION

Kinetic studies of H(I)—metal-ion exchanges on ion-exchange materials are important for their economic and industrial applications. The Bt criterion proposed by Boyd et al. [1] is useful for ions having similar effective diffusion coefficients, i.e. for an isotopic exchange process. In a true ion-exchange phenomenon, however, the fluxes of at least two different ionic species are coupled with one another. Thus, a single diffusion coefficient cannot describe the actual process. In such a case, the non-linear Nernst—Planck equations [2, 3] should be applicable for a particle diffusion-controlled ion exchange with some additional assumptions [4]. For practical purposes, an explicit expression was given by Helfferich et al. [5, 6] which approximates the numerical results. Using this expression we have evaluated earlier [7—14] the dimensionless time parameter (τ) for some systems applying the graphical method for its solution. However, the graphical method has been found tedious and gives only the approximate τ values resulting in less accurate kinetic parameters. In view of this the present study has been undertaken to evaluate the τ values for a number of cases involving the exchange of H(I) with bivalent ions using a computer, thus simplifying the treatment and improving the accuracy of the results.

0166-6622/86/$03.50

TABLE 1

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion-controlled H(I)—metal(II) exchanges involving different mobility ratios

Fractional *attainment* of equilibrium, $U(\tau)$	Dimensionless time, τ				
	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Mn}}$ = 11.39	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Co}}$ = 7.42	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Ni}}$ = 7.25	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Fe/Cr}}$ = 7.09	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Mg/Cu}}$ = 6.95
0.01	2.501×10^{-5}	2.040×10^{-5}	2.019×10^{-5}	1.998×10^{-5}	1.980×10^{-5}
0.05	6.262×10^{-4}	5.106×10^{-4}	5.053×10^{-4}	5.002×10^{-4}	4.957×10^{-4}
0.10	2.516×10^{-3}	2.052×10^{-3}	2.030×10^{-3}	2.010×10^{-3}	1.992×10^{-3}
0.15	5.706×10^{-3}	4.651×10^{-3}	4.603×10^{-3}	4.556×10^{-3}	4.516×10^{-3}
0.20	1.026×10^{-2}	8.358×10^{-3}	8.271×10^{-3}	8.187×10^{-3}	8.114×10^{-3}
0.25	1.626×10^{-2}	1.324×10^{-2}	1.311×10^{-2}	1.297×10^{-2}	1.286×10^{-2}
0.30	2.384×10^{-2}	1.941×10^{-2}	1.920×10^{-2}	1.901×10^{-2}	1.884×10^{-2}
0.35	3.315×10^{-2}	2.697×10^{-2}	2.669×10^{-2}	2.642×10^{-2}	2.618×10^{-2}
0.40	4.441×10^{-2}	3.611×10^{-2}	3.573×10^{-2}	3.537×10^{-2}	3.505×10^{-2}
0.45	5.789×10^{-2}	4.705×10^{-2}	4.655×10^{-2}	4.608×10^{-2}	4.566×10^{-2}
0.50	7.395×10^{-2}	6.006×10^{-2}	5.943×10^{-2}	5.882×10^{-2}	5.829×10^{-2}
0.55	9.303×10^{-2}	7.551×10^{-2}	7.472×10^{-2}	7.395×10^{-2}	7.328×10^{-2}
0.60	1.157×10^{-1}	9.389×10^{-2}	9.290×10^{-2}	9.194×10^{-2}	9.111×10^{-2}
0.65	1.428×10^{-1}	1.158×10^{-1}	1.146×10^{-1}	1.134×10^{-1}	1.124×10^{-1}
0.70	1.752×10^{-1}	1.422×10^{-1}	1.407×10^{-1}	1.393×10^{-1}	1.380×10^{-1}
0.75	2.143×10^{-1}	1.743×10^{-1}	1.724×10^{-1}	1.707×10^{-1}	1.692×10^{-1}
0.80	2.620×10^{-1}	2.137×10^{-1}	2.115×10^{-1}	2.094×10^{-1}	2.076×10^{-1}
0.85	3.216×10^{-1}	2.636×10^{-1}	2.609×10^{-1}	2.584×10^{-1}	2.561×10^{-1}
0.90	3.990×10^{-1}	3.295×10^{-1}	3.263×10^{-1}	3.233×10^{-1}	3.206×10^{-1}
0.95	5.124×10^{-1}	4.279×10^{-1}	4.240×10^{-1}	4.202×10^{-1}	4.170×10^{-1}
0.99	7.067×10^{-1}	5.994×10^{-1}	5.944×10^{-1}	5.896×10^{-1}	5.854×10^{-1}

Fractional attainment of equilibrium, $U(\tau)$	Dimensionless time, τ				
	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Cd}}$ = 6.87	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Zn}}$ = 6.79	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Sr/Ca}}$ = 6.14	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Ba}}$ = 5.76	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Pb}}$ = 5.25
0.01	1.971×10^{-5}	1.960×10^{-5}	1.876×10^{-5}	1.823×10^{-5}	1.752×10^{-5}
0.05	4.933×10^{-4}	4.905×10^{-4}	4.695×10^{-4}	4.564×10^{-4}	4.387×10^{-4}
0.10	1.982×10^{-3}	1.971×10^{-3}	1.886×10^{-3}	1.834×10^{-3}	1.762×10^{-3}
0.15	4.494×10^{-3}	4.468×10^{-3}	4.276×10^{-3}	4.157×10^{-3}	3.995×10^{-3}
0.20	8.075×10^{-3}	8.028×10^{-3}	7.683×10^{-3}	7.468×10^{-3}	7.178×10^{-3}
0.25	1.279×10^{-2}	1.272×10^{-2}	1.217×10^{-2}	1.183×10^{-2}	1.137×10^{-2}
0.30	1.875×10^{-2}	1.864×10^{-2}	1.783×10^{-2}	1.733×10^{-2}	1.666×10^{-2}
0.35	2.605×10^{-2}	2.590×10^{-2}	2.478×10^{-2}	2.409×10^{-2}	2.315×10^{-2}
0.40	3.488×10^{-2}	3.468×10^{-2}	3.318×10^{-2}	3.224×10^{-2}	3.098×10^{-2}
0.45	4.544×10^{-2}	4.517×10^{-2}	4.322×10^{-2}	4.200×10^{-2}	4.035×10^{-2}
0.50	5.800×10^{-2}	5.766×10^{-2}	5.516×10^{-2}	5.360×10^{-2}	5.150×10^{-2}
0.55	7.292×10^{-2}	7.249×10^{-2}	6.934×10^{-2}	6.738×10^{-2}	6.474×10^{-2}
0.60	9.066×10^{-2}	9.014×10^{-2}	8.621×10^{-2}	8.378×10^{-2}	8.049×10^{-2}
0.65	1.119×10^{-1}	1.112×10^{-1}	1.064×10^{-1}	1.034×10^{-1}	9.933×10^{-2}
0.70	1.374×10^{-1}	1.366×10^{-1}	1.306×10^{-1}	1.270×10^{-1}	1.220×10^{-1}
0.75	1.683×10^{-1}	1.674×10^{-1}	1.602×10^{-1}	1.557×10^{-1}	1.497×10^{-1}
0.80	2.066×10^{-1}	2.054×10^{-1}	1.967×10^{-1}	1.913×10^{-1}	1.840×10^{-1}
0.85	2.549×10^{-1}	2.535×10^{-1}	2.431×10^{-1}	2.365×10^{-1}	2.278×10^{-1}
0.90	3.191×10^{-1}	3.174×10^{-1}	3.048×10^{-1}	2.970×10^{-1}	2.863×10^{-1}
0.95	4.152×10^{-1}	4.131×10^{-1}	3.977×10^{-1}	3.880×10^{-1}	3.750×10^{-1}
0.99	5.832×10^{-1}	5.805×10^{-1}	5.607×10^{-1}	5.484×10^{-1}	5.317×10^{-1}

TABLE 2

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion-controlled metal(II)—H(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium, $U(\tau)$	Dimensionless time, τ				
	$\alpha = \frac{\bar{D}_{Mn}}{\bar{D}_H}$ = 0.088	$\alpha = \frac{\bar{D}_{Co}}{\bar{D}_H}$ = 0.135	$\alpha = \frac{\bar{D}_{Ni}}{\bar{D}_H}$ = 0.138	$\alpha = \frac{\bar{D}_{Fe/Cr}}{\bar{D}_H}$ = 0.141	$\alpha = \frac{\bar{D}_{Mg/Cu}}{\bar{D}_H}$ = 0.144
0.01	4.360×10^{-6}	4.723×10^{-6}	4.747×10^{-6}	4.770×10^{-6}	4.791×10^{-6}
0.05	1.093×10^{-4}	1.183×10^{-4}	1.189×10^{-4}	1.195×10^{-4}	1.200×10^{-4}
0.10	4.404×10^{-4}	4.768×10^{-4}	4.792×10^{-4}	4.815×10^{-4}	4.836×10^{-4}
0.15	1.004×10^{-3}	1.086×10^{-3}	1.092×10^{-3}	1.097×10^{-3}	1.102×10^{-3}
0.20	1.817×10^{-3}	1.966×10^{-3}	1.975×10^{-3}	1.985×10^{-3}	1.993×10^{-3}
0.25	2.909×10^{-3}	3.143×10^{-3}	3.158×10^{-3}	3.173×10^{-3}	3.187×10^{-3}
0.30	4.319×10^{-3}	4.661×10^{-3}	4.682×10^{-3}	4.704×10^{-3}	4.723×10^{-3}
0.35	6.102×10^{-3}	6.575×10^{-3}	6.604×10^{-3}	6.634×10^{-3}	6.660×10^{-3}
0.40	8.336×10^{-3}	8.964×10^{-3}	9.002×10^{-3}	9.041×10^{-3}	9.075×10^{-3}
0.45	1.113×10^{-2}	1.193×10^{-2}	1.198×10^{-2}	1.203×10^{-2}	1.208×10^{-2}
0.50	1.462×10^{-2}	1.563×10^{-2}	1.569×10^{-2}	1.575×10^{-2}	1.580×10^{-2}
0.55	1.901×10^{-2}	2.024×10^{-2}	2.031×10^{-2}	2.038×10^{-2}	2.045×10^{-2}
0.60	2.449×10^{-2}	2.597×10^{-2}	2.606×10^{-2}	2.615×10^{-2}	2.622×10^{-2}
0.65	3.524×10^{-2}	3.302×10^{-2}	3.312×10^{-2}	3.323×10^{-2}	3.332×10^{-2}
0.70	3.921×10^{-2}	4.177×10^{-2}	4.191×10^{-2}	4.205×10^{-2}	4.218×10^{-2}
0.75	4.981×10^{-2}	5.250×10^{-2}	5.267×10^{-2}	5.284×10^{-2}	5.299×10^{-2}
0.80	6.371×10^{-2}	6.692×10^{-2}	6.712×10^{-2}	6.732×10^{-2}	6.750×10^{-2}
0.85	8.387×10^{-2}	8.761×10^{-2}	8.784×10^{-2}	8.808×10^{-2}	8.829×10^{-2}
0.90	1.169×10^{-1}	1.209×10^{-1}	1.211×10^{-1}	1.214×10^{-1}	1.216×10^{-1}
0.95	1.849×10^{-1}	1.874×10^{-1}	1.875×10^{-1}	1.877×10^{-1}	1.878×10^{-1}
0.99	3.310×10^{-1}	3.338×10^{-1}	3.337×10^{-1}	3.336×10^{-1}	3.336×10^{-1}

Fractional attainment of equilibrium, $U(\tau)$	Dimensionless time, τ				
	$\alpha = \frac{\bar{D}_{Cd}}{\bar{D}_H}$ = 0.146	$\alpha = \frac{\bar{D}_{Zn}}{\bar{D}_H}$ = 0.147	$\alpha = \frac{\bar{D}_{Sr/Ca}}{\bar{D}_H}$ = 0.163	$\alpha = \frac{\bar{D}_{Ba}}{\bar{D}_H}$ = 0.174	$\alpha = \frac{\bar{D}_{Pb}}{\bar{D}_H}$ = 0.191
0.01	4.803×10^{-6}	4.817×10^{-6}	4.930×10^{-6}	5.009×10^{-6}	5.131×10^{-6}
0.05	1.203×10^{-4}	1.207×10^{-4}	1.235×10^{-4}	1.255×10^{-4}	1.285×10^{-4}
0.10	4.848×10^{-4}	4.862×10^{-4}	4.975×10^{-4}	5.055×10^{-4}	5.177×10^{-4}
0.15	1.104×10^{-3}	1.107×10^{-3}	1.133×10^{-3}	1.151×10^{-3}	1.178×10^{-3}
0.20	1.998×10^{-3}	2.003×10^{-3}	2.049×10^{-3}	2.081×10^{-3}	2.130×10^{-3}
0.25	3.194×10^{-3}	3.203×10^{-3}	3.274×10^{-3}	3.324×10^{-3}	3.400×10^{-3}
0.30	4.734×10^{-3}	4.747×10^{-3}	4.849×10^{-3}	4.925×10^{-3}	5.031×10^{-3}
0.35	6.674×10^{-3}	6.692×10^{-3}	6.832×10^{-3}	6.930×10^{-3}	7.078×10^{-3}
0.40	9.904×10^{-3}	9.117×10^{-3}	9.299×10^{-3}	9.426×10^{-3}	9.618×10^{-3}
0.45	1.210×10^{-2}	1.213×10^{-2}	1.236×10^{-2}	1.252×10^{-2}	1.276×10^{-2}
0.50	1.583×10^{-2}	1.587×10^{-2}	1.615×10^{-2}	1.634×10^{-2}	1.663×10^{-2}
0.55	2.048×10^{-2}	2.052×10^{-2}	2.086×10^{-2}	2.108×10^{-2}	2.143×10^{-2}
0.60	2.626×10^{-2}	2.631×10^{-2}	2.671×10^{-2}	2.698×10^{-2}	2.738×10^{-2}
0.65	3.337×10^{-2}	3.343×10^{-2}	3.391×10^{-2}	3.424×10^{-2}	3.473×10^{-2}
0.70	4.225×10^{-2}	4.233×10^{-2}	4.301×10^{-2}	4.348×10^{-2}	4.420×10^{-2}
0.75	5.308×10^{-2}	5.318×10^{-2}	5.399×10^{-2}	5.457×10^{-2}	5.544×10^{-2}
0.80	6.760×10^{-2}	6.772×10^{-2}	6.870×10^{-2}	6.938×10^{-2}	7.042×10^{-2}
0.85	8.841×10^{-2}	8.855×10^{-2}	8.968×10^{-2}	9.048×10^{-2}	9.170×10^{-2}
0.90	1.217×10^{-1}	1.219×10^{-1}	1.231×10^{-1}	1.239×10^{-1}	1.253×10^{-1}
0.95	1.878×10^{-1}	1.879×10^{-1}	1.886×10^{-1}	1.892×10^{-1}	1.901×10^{-1}
0.99	3.335×10^{-1}	3.335×10^{-1}	3.329×10^{-1}	3.326×10^{-1}	3.321×10^{-1}

RESULTS AND DISCUSSION

According to the explicit approximation given by Helfferich et al. [5, 6], the fractional attainment of equilibrium for a particle diffusion-controlled phenomenon is given by

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \quad (1)$$

where $\tau = \bar{D}_A t/r_0^2$ and mobility ratio, $\alpha = \bar{D}_A/\bar{D}_B$. The coefficients $\bar{D}_A$ and $\bar{D}_B$ are the diffusion coefficients of counter ions A and B, respectively, in the ion-exchanger phase, r_0 is the bead radius and t is the time. If the ion exchanger is taken in the H(I) form and the exchanging ion is M(II), then for $1 \leqslant \alpha \leqslant 20$

$$f_1(\alpha) = -1/(0.64 + 0.36\alpha^{0.668})$$

$$f_2(\alpha) = -1/(0.96 - 2.0\alpha^{0.4635})$$

$$f_3(\alpha) = -1/(0.27 + 0.09\alpha^{1.14})$$

In the reverse process, i.e. when the ion-exchanger is in the M(II) form and the exchanging ion is H(I), we have

$$f_1(\alpha) = -1/(0.350 + 0.650\alpha^{0.860})$$

$$f_2(\alpha) = 1/(0.030 + 1.012\alpha^{2.06})$$

$$f_3(\alpha) = -1/(0.00265 + 0.354\alpha^{2.671})$$

for $0.05 \leqslant \alpha \leqslant 1$ and $0 \leqslant \tau \leqslant 0.04$, and

$$f_1(\alpha) = -1/(0.438 + 0.562\alpha^{0.777})$$

$$f_2(\alpha) = 1/(0.127 + 0.915\alpha^{1.057})$$

$$f_3(\alpha) = 1/(0.008 - 0.365\alpha^{0.453})$$

for $0.05 \leqslant \alpha \leqslant 1$ and $\tau \geqslant 0.04$.

The r values obtained from Eqn (1) for the forward and reverse exchange of H(I) with some bivalent metal ions are given in Tables 1 and 2, respectively, for the various fractional exchange values. A computer, Model VAX-11/780 manufactured by the Digital Equipment Corporation, Maynard, MA, was used for calculations.

ACKNOWLEDGEMENTS

Dr Tariq Aziz is thanked for his valuable suggestions and the Council of Scientific and Industrial Research, New Delhi (India) for financial assistance.

REFERENCES

1 G.E. Boyd, A.W. Adamson and L.S. Myers, J. Am. Chem. Soc., 69 (1947) 2836.
2 W.Z. Nernst, Z. Phys. Chem., 2 (1888) 613; 4 (1889) 729.
3 M. Planck, Ann. Phys. Chem., 39 (1890) 161.
4 F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962, Ch. 6.
5 F. Helfferich and M.S. Plesset., J. Chem. Phys., 28 (1958) 418.
6. M.S. Plesset, F. Helfferich and J.N. Franklin, J. Chem. Phys., 29 (1958) 1064.
7 K.G. Varshney, S. Agrawal and K. Varshney, Acta Chim. Hung., 116 (1984) 69.
8 K.G. Varshney, S. Agrawal and K. Varshney, Colloids Surfaces, 9 (1984) 189.
9 K.G. Varshney, A.A. Khan, K. Varshney and S. Agrawal, Solvent Extr. Ion Exch., 2 (1984) 923.
10 K.G. Varshney and S. Rani, Indian. J. Chem., 22A (1983) 657.
11 K.G. Varshney and U. Sharma, Acta Chim. Hung., 116 (1984) 103.
12 K.G. Varshney, U. Sharma, S. Anwar and A.A. Khan, Indian J. Chem., 23A (1984) 152.
13 K.G. Varshney and U. Sharma, React. Kinet. Catal. lett., 28 (1985) 27.
14 K.G. Varshney, S. Agrawal and K. Varshney, Colloids Surfaces, 13 (1985) 341.

Colloids and Surfaces (In Press)

3.12 EVALUATION OF THE DIMENSIONLESS TIME PARAMETER FOR SOME PARTICLE DIFFUSION CONTROLLED FORWARD AND REVERSE OH(I)-ANION(I) AND OH(I)-ANION(II) EXCHANGES

KRISHNA GOPAL VARSHNEY, ASHFAQ RABBANI KHAN AND KHWAJA ZUBER ALAM
Department of Applied Chemistry,
Z.H.College of Engineering & Technology,
Aligarh Muslim University,
Aligarh-202002 (India)

AND

ANEES AHMAD
Department of Chemistry,
Aligarh Muslim University,
Aligarh-202002 (India).

INTRODUCTION

Energy and entropy of activation are the fundamental properties of a system. These parameters are important to understand the mechanism of interactions during the adsorption or ion exchange which are intermixed in case of inorganic ion exchanger. In a true ion exchange phenomenon, different mobilities (1) of the exchanging ions are involved and hence for such a case Nernst-Planck equations (2,3) give the precise values of the various kinetic parameters. For practical purposes, an explicit expression was given by Helfferich et al. (1,4). Using this expression we have evaluated earlier (5-14) the dimensionless time parameter ($\tilde{\tau}$) for some systems applying the graphical method for its solution. It was noticed that this method was very tedious and gave only the approximate $\tilde{\tau}$ values. A computer simulation technique has,

therefore, been used. On the basis of which we have earlier reported (15) the τ values for the particle diffusion controlled forward and reverse H(I)-Metal(II) ion exchanges. In continuation we, here, report the τ values obtained for the exchange of OH(I) ions with some common mono- and bi-valent anions, using a computer which improves the results accuracy. A knowledge of τ values for the various mobility ratios is very important and makes the calculations much easier for the evaluation of the kinetic parameters. The present report will help in the study of anion exchanges.

RESULTS AND DISCUSSION

According to the explicit approximation given by Helferrich et al. (1,4) the fractional attainment of equilibrium for a particle diffusion controlled phenomenon is given by

$$U_{(\tau)} = \left[1-\exp\left\{\pi^2\left(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3\right)\right\}\right]^{\frac{1}{2}} \quad \ldots\ldots \quad (1)$$

where $\tau = \bar{D}_A t/r_o$ and $\alpha = \bar{D}_A/\bar{D}_B$. The coefficients $\bar{D}_A$ and $\bar{D}_B$ are the diffusion coefficients of counter ions A and B respectively in the ion exchanger phase, r_o is the bead radius and t is the time.

<u>For monovalent anions A(I)</u>: A monovalent anion exchange phenomenon may be expressed as follows:

$$R^+OH^- + A^- \rightleftharpoons R^+A^- + OH^-$$

For the above process both in the forward and reverse directions the coefficients are given by

$$f_1(\alpha) = 1/(0.57 + 0.43\alpha^{0.775})$$
$$f_2(\alpha) = 1/(0.26 + 0.788\alpha)$$
$$f_3(\alpha) = 1/(0.165 + 0.177\alpha)$$

for a range of validity $0.1 \leqslant \alpha \leqslant 10$.

For bivalent anions: A bivalent anion exchange equation may be given as

$$2R^{+}OH^{-} + A^{2-} \rightleftharpoons R_2^{+}A^{2-} + 2OH^{-}$$

For the forward process i.e. if the ion exchanger is taken in OH(I) form and the exchanging ion is A(II) then the coefficients are given by for a range of $1 \leqslant \alpha \leqslant 20$

$$f_1(\alpha) = -1/(0.64 + 0.36\alpha^{0.668})$$
$$f_2(\alpha) = -1/(0.96 - 2.0\alpha^{0.4635})$$
$$f_3(\alpha) = -1/(0.27 + 0.09\alpha^{1.14})$$

and for the reverse process i.e. when the ion exchanger is in A(II) form and the exchanging ion is OH(I) then we have

$$f_1(\alpha) = -1/(0.35 + 0.65\alpha^{0.86})$$
$$f_2(\alpha) = -1/(0.03 + 1.012\alpha^{2.06})$$
$$f_3(\alpha) = -1/(0.00265 + 0.354\alpha^{2.671})$$

for the range of $0.05 \leqslant \alpha \leqslant 1$ and $0 \leqslant \tau \leqslant 0.04$ and

$$f_1(\alpha) = -1/(0.438 + 0.562\,\alpha^{0.777})$$

$$f_2(\alpha) = 1/(0.127 + 0.915\alpha^{1.057})$$

$$f_3(\alpha) = 1/(0.008 - 0.365\alpha^{0.453})$$

for $0.05 \leqslant \alpha \leqslant 1$ and $\tau > 0.04$

The α values obtained from equation (1) for the forward and reverse exchange of OH(I) with some monovalent and bivalent anions are given in Tables 1-4 respectively for the various fractional exchange values. A computer, model VAX 11/780 manufactured by the digital equipment corporation, Maynard,MA was used for these calculations.

ACKNOWLEDGEMENT

Prof. K.T.Nasim, Chairman, Department of Applied Chemistry and Director of Computer Centre, Aligarh Muslim University, Aligarh are thanked for providing research facilities.

REFERENCES

1 F.Helfferich "Ion Exchange", McGraw Hill Book Co., New York 1962 Ch. 6.

2 W.Nernst, Z.Physik.Chem., 2 (1888) 1613; 4 (1889) 729.

3 M.Planek, Ann.Phys.Chem., 39 (1890) 161.

4 M.S.Plesset, F.Helfferich and J.N.Franklin, J.Chem.Phys., 29 (1958) 1064.

5 K.G.Varshney, S.Agrawal and K.Varshney, Acta.Chim.Hung., 116 (1984) 69.

6 K.G.Varshney, S.Agrawal and K.Varshney, Colloids Surfaces, 9 (1984), 189.

7 K.G.Varshney, A.A.Khan, K.Varshney and S.Agrawal, Solvent Extra.Ion Exch., 2 (1984), 923.

8 K.G.Varshney and S.Rani, Ind.J.Chem., 22A (1983) 657.

9 K.G.Varshney and U.Sharma, Acta Chim.Hung., 116 (1984) 103.

10 K.G.Varshney, U.Sharma, S.Anwar and A.A.Khan, Indian J.Chem., 23A (1984) 152.

11 K.G.Varshney and U.Sharma, React.Kinet.Catal.Lett., 28 (1985) 27.

12 K.G.Varshney, S.Agrawal and K.Varshney, Colloids Surfaces, 13 (1985) 341.

13 K.G.Varshney, A.A.Khan and A.R.Khan, Bull.Chem.Soc.Jpn., 61 (1988) 3693.

14 K.G.Varshney, S.Agrawal, K.Agrawal, V.Saxena and A.R.Khan, Colloids Surfaces, 29 (1988) 175.

15 K.G.Varshney, K.Varshney and S.Agrawal, Colloids Surfaces, 18 (1986) 67.

TABLE 1

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled OH(I)-A(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ						
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{IO_3}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{F}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{BrO_3}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{MnO_4}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{ClO_3/CNO/OCN}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SCN}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{ClO_4}}$
	= 4.889	= 3.574	= 3.554	= 3.230	= 3.065	= 3.000	= 2.942
0.01	2.068×10^{-5}	1.747×10^{-5}	1.742×10^{-5}	1.659×10^{-5}	1.616×10^{-5}	1.599×10^{-5}	1.583×10^{-5}
0.05	5.178×10^{-4}	4.373×10^{-4}	4.360×10^{-4}	4.152×10^{-4}	4.045×10^{-4}	4.002×10^{-4}	3.963×10^{-4}
0.10	2.081×10^{-3}	1.757×10^{-3}	1.752×10^{-3}	1.668×10^{-3}	1.625×10^{-3}	1.606×10^{-3}	1.593×10^{-3}
0.15	4.717×10^{-3}	3.984×10^{-3}	3.972×10^{-3}	3.782×10^{-3}	3.684×10^{-3}	3.645×10^{-3}	3.610×10^{-3}
0.20	8.477×10^{-3}	7.158×10^{-3}	7.138×10^{-3}	6.797×10^{-3}	6.620×10^{-3}	6.550×10^{-3}	6.687×10^{-3}
0.25	1.343×10^{-2}	1.134×10^{-2}	1.131×10^{-2}	1.077×10^{-2}	1.049×10^{-2}	1.038×10^{-2}	1.028×10^{-2}
0.30	1.968×10^{-2}	1.662×10^{-2}	1.657×10^{-2}	1.578×10^{-2}	1.537×10^{-2}	1.521×10^{-2}	1.506×10^{-2}
0.35	2.736×10^{-2}	2.310×10^{-2}	2.303×10^{-2}	2.193×10^{-2}	2.136×10^{-2}	2.114×10^{-2}	2.093×10^{-2}
0.40	3.663×10^{-2}	3.093×10^{-2}	3.084×10^{-2}	2.937×10^{-2}	2.860×10^{-2}	2.830×10^{-2}	2.803×10^{-2}
0.45	4.772×10^{-2}	4.030×10^{-2}	4.0184×10^{-2}	3.826×10^{-2}	3.727×10^{-2}	3.688×10^{-2}	3.652×10^{-2}
0.50	6.092×10^{-2}	5.145×10^{-2}	5.130×10^{-2}	4.885×10^{-2}	4.759×10^{-2}	4.709×10^{-2}	4.664×10^{-2}
0.55	7.654×10^{-2}	6.470×10^{-2}	6.451×10^{-2}	6.145×10^{-2}	5.986×10^{-2}	5.923×10^{-2}	5.867×10^{-2}
0.60	9.511×10^{-2}	8.048×10^{-2}	8.025×10^{-2}	7.646×10^{-2}	7.449×10^{-2}	7.371×10^{-2}	7.301×10^{-2}
0.65	1.172×10^{-1}	9.935×10^{-2}	9.907×10^{-2}	9.443×10^{-2}	9.202×10^{-2}	9.106×10^{-2}	9.021×10^{-2}
0.70	1.437×10^{-1}	1.221×10^{-1}	1.217×10^{-1}	1.161×10^{-1}	1.132×10^{-1}	1.120×10^{-1}	1.110×10^{-1}
0.75	1.756×10^{-1}	1.498×10^{-1}	1.494×10^{-1}	1.426×10^{-1}	1.391×10^{-1}	1.377×10^{-1}	1.364×10^{-1}
0.80	2.147×10^{-1}	1.841×10^{-1}	1.836×10^{-1}	1.755×10^{-1}	1.713×10^{-1}	1.696×10^{-1}	1.661×10^{-1}
0.85	2.636×10^{-1}	2.277×10^{-1}	2.271×10^{-1}	2.175×10^{-1}	2.175×10^{-1}	2.106×10^{-1}	2.088×10^{-1}
0.90	3.275×10^{-1}	2.857×10^{-1}	2.850×10^{-1}	2.739×10^{-1}	2.680×10^{-1}	2.657×10^{-1}	2.636×10^{-1}
0.95	4.217×10^{-1}	3.780×10^{-1}	3.722×10^{-1}	3.590×10^{-1}	3.521×10^{-1}	3.493×10^{-1}	3.468×10^{-1}
0.99	5.848×10^{-1}	5.259×10^{-1}	5.249×10^{-1}	5.089×10^{-1}	5.005×10^{-1}	4.972×10^{-1}	4.941×10^{-1}

(Table 1 continued)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{NO_3}}$ = 2.772	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{NO_2}}$ = 2.757	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{Cl}}$ = 2.595	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{I}}$ = 2.578	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{CN}}$ = 2.538	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{Br}}$ = 2.535
0.01	1.538×10^{-5}	1.534×10^{-5}	1.490×10^{-5}	1.486×10^{-5}	1.475×10^{-5}	1.474×10^{-5}
0.05	3.850×10^{-4}	3.840×10^{-4}	3.730×10^{-4}	3.718×10^{-4}	3.691×10^{-4}	3.689×10^{-4}
0.10	1.547×10^{-3}	1.543×10^{-3}	1.499×10^{-3}	1.494×10^{-3}	1.483×10^{-3}	1.482×10^{-3}
0.15	3.507×10^{-3}	3.498×10^{-3}	3.398×10^{-3}	3.387×10^{-3}	3.362×10^{-3}	3.360×10^{-3}
0.20	6.301×10^{-3}	6.285×10^{-3}	6.105×10^{-3}	6.086×10^{-3}	6.041×10^{-3}	6.038×10^{-3}
0.25	9.984×10^{-3}	9.958×10^{-3}	9.673×10^{-3}	9.643×10^{-3}	9.572×10^{-3}	9.566×10^{-3}
0.30	1.463×10^{-2}	1.459×10^{-2}	1.417×10^{-2}	1.413×10^{-2}	1.402×10^{-2}	1.402×10^{-2}
0.35	2.033×10^{-2}	2.028×10^{-2}	1.970×10^{-2}	1.964×10^{-2}	1.949×10^{-2}	1.948×10^{-2}
0.40	2.723×10^{-2}	2.716×10^{-2}	2.638×10^{-2}	2.630×10^{-2}	2.610×10^{-2}	2.609×10^{-2}
0.45	3.548×10^{-2}	3.538×10^{-2}	3.437×10^{-2}	3.427×10^{-2}	3.401×10^{-2}	3.400×10^{-2}
0.50	4.530×10^{-2}	4.519×10^{-2}	4.390×10^{-2}	4.376×10^{-2}	4.344×10^{-2}	4.342×10^{-2}
0.55	5.700×10^{-2}	5.685×10^{-2}	5.523×10^{-2}	5.506×10^{-2}	5.466×10^{-2}	5.463×10^{-2}
0.60	7.094×10^{-2}	7.076×10^{-2}	6.876×10^{-2}	6.855×10^{-2}	6.805×10^{-2}	6.801×10^{-2}
0.65	8.767×10^{-2}	8.744×10^{-2}	8.499×10^{-2}	8.473×10^{-2}	8.412×10^{-2}	8.407×10^{-2}
0.70	1.079×10^{-1}	1.076×10^{-1}	1.047×10^{-1}	1.043×10^{-1}	1.036×10^{-1}	1.035×10^{-1}
0.75	1.327×10^{-1}	1.324×10^{-1}	1.288×10^{-1}	1.284×10^{-1}	1.275×10^{-1}	1.274×10^{-1}
0.80	1.637×10^{-1}	1.633×10^{-1}	1.590×10^{-1}	1.585×10^{-1}	1.574×10^{-1}	1.574×10^{-1}
0.85	2.035×10^{-1}	2.030×10^{-1}	1.979×10^{-1}	1.973×10^{-1}	1.961×10^{-1}	1.960×10^{-1}
0.90	2.573×10^{-1}	2.568×10^{-1}	2.507×10^{-1}	2.500×10^{-1}	2.485×10^{-1}	2.484×10^{-1}
0.95	3.394×10^{-1}	3.388×10^{-1}	3.316×10^{-1}	3.308×10^{-1}	3.290×10^{-1}	3.289×10^{-1}
0.99	4.851×10^{-1}	4.843×10^{-1}	4.755×10^{-1}	4.746×10^{-1}	4.724×10^{-1}	4.722×10^{-1}

TABLE 2

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled A(I)-OH(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ						
	$\alpha = \frac{\bar{D}_{IO_3}}{\bar{D}_{OH}}$ = 0.204	$\alpha = \frac{\bar{D}_{F}}{\bar{D}_{OH}}$ = 0.279	$\alpha = \frac{\bar{D}_{BrO_3}}{\bar{D}_{OH}}$ = 0.281	$\alpha = \frac{\bar{D}_{MnO_4}}{\bar{D}_{OH}}$ = 0.309	$\alpha = \frac{\bar{D}_{ClO_3/CNO/OCN}}{\bar{D}_{OH}}$ = 0.326	$\alpha = \frac{\bar{D}_{SCN}}{\bar{D}_{OH}}$ = 0.334	$\alpha = \frac{\bar{D}_{ClO_4}}{\bar{D}_{OH}}$ = 0.339
0.01	7.048×10^{-6}	7.397×10^{-6}	7.406×10^{-6}	7.530×10^{-6}	7.605×10^{-6}	7.639×10^{-6}	7.661×10^{-6}
0.05	1.764×10^{-4}	1.852×10^{-4}	1.854×10^{-4}	1.885×10^{-4}	1.904×10^{-4}	1.912×10^{-4}	1.918×10^{-4}
0.10	7.090×10^{-4}	7.441×10^{-4}	7.450×10^{-4}	7.575×10^{-4}	7.650×10^{-4}	7.685×10^{-4}	7.706×10^{-4}
0.15	1.608×10^{-3}	1.687×10^{-3}	1.689×10^{-3}	1.718×10^{-3}	1.735×10^{-3}	1.742×10^{-3}	1.747×10^{-3}
0.20	2.890×10^{-3}	3.033×10^{-3}	3.037×10^{-3}	3.087×10^{-3}	3.118×10^{-3}	3.132×10^{-3}	3.141×10^{-3}
0.25	4.582×10^{-3}	4.808×10^{-3}	4.814×10^{-3}	4.894×10^{-3}	4.942×10^{-3}	4.964×10^{-3}	4.978×10^{-3}
0.30	6.719×10^{-3}	7.049×10^{-3}	7.058×10^{-3}	7.175×10^{-3}	7.246×10^{-3}	7.278×10^{-3}	7.299×10^{-3}
0.35	9.350×10^{-3}	9.808×10^{-3}	9.819×10^{-3}	9.983×10^{-3}	1.008×10^{-2}	1.013×10^{-2}	1.015×10^{-2}
0.40	1.254×10^{-2}	1.315×10^{-2}	1.317×10^{-2}	1.338×10^{-2}	1.351×10^{-2}	1.357×10^{-2}	1.361×10^{-2}
0.45	1.637×10^{-2}	1.717×10^{-2}	1.719×10^{-2}	1.747×10^{-2}	1.764×10^{-2}	1.772×10^{-2}	1.777×10^{-2}
0.50	2.097×10^{-2}	2.198×10^{-2}	2.200×10^{-2}	2.236×10^{-2}	2.258×10^{-2}	2.268×10^{-2}	2.274×10^{-2}
0.55	2.648×10^{-2}	2.774×10^{-2}	2.778×10^{-2}	2.823×10^{-2}	2.850×10^{-2}	2.862×10^{-2}	2.870×10^{-2}
0.60	3.314×10^{-2}	3.470×10^{-2}	3.474×10^{-2}	3.530×10^{-2}	3.563×10^{-2}	3.578×10^{-2}	3.588×10^{-2}
0.65	4.127×10^{-2}	4.317×10^{-2}	4.322×10^{-2}	4.391×10^{-2}	4.431×10^{-2}	4.450×10^{-2}	4.462×10^{-2}
0.70	5.135×10^{-2}	5.367×10^{-2}	5.373×10^{-2}	5.455×10^{-2}	5.505×10^{-2}	5.528×10^{-2}	5.542×10^{-2}
0.75	6.416×10^{-2}	6.696×10^{-2}	6.703×10^{-2}	6.803×10^{-2}	6.863×10^{-2}	6.891×10^{-2}	6.908×10^{-2}
0.80	8.103×10^{-2}	8.438×10^{-2}	8.446×10^{-2}	8.566×10^{-2}	8.638×10^{-2}	8.671×10^{-2}	8.692×10^{-2}
0.85	1.045×10^{-1}	1.084×10^{-1}	1.085×10^{-1}	1.099×10^{-1}	1.108×10^{-1}	1.112×10^{-1}	1.114×10^{-1}
0.90	1.400×10^{-1}	1.444×10^{-1}	1.445×10^{-1}	1.461×10^{-1}	1.471×10^{-1}	1.475×10^{-1}	1.478×10^{-1}
0.95	2.035×10^{-1}	2.074×10^{-1}	2.076×10^{-1}	2.091×10^{-1}	2.101×10^{-1}	2.105×10^{-1}	2.108×10^{-1}
0.99	3.322×10^{-1}	3.332×10^{-1}	3.332×10^{-1}	3.341×10^{-1}	3.347×10^{-1}	3.350×10^{-1}	3.352×10^{-1}

(Table 2 continued)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{NO_3}}{\bar{D}_{OH}}$ = 0.361	$\alpha = \frac{\bar{D}_{NO_2}}{\bar{D}_{OH}}$ = 0.363	$\alpha = \frac{\bar{D}_{Cl}}{\bar{D}_{OH}}$ = 0.385	$\alpha = \frac{\bar{D}_{I}}{\bar{D}_{OH}}$ = 0.387	$\alpha = \frac{\bar{D}_{CN}}{\bar{D}_{OH}}$ = 0.394	$\alpha = \frac{\bar{D}_{Br}}{\bar{D}_{OH}}$ = 0.395
0.01	7.755×10^{-6}	7.764×10^{-6}	7.856×10^{-6}	7.865×10^{-6}	7.898×10^{-6}	7.898×10^{-6}
0.05	1.941×10^{-4}	1.943×10^{-4}	1.967×10^{-4}	1.969×10^{-4}	1.976×10^{-4}	1.977×10^{-4}
0.10	7.801×10^{-4}	7.809×10^{-4}	7.903×10^{-4}	7.911×10^{-4}	7.940×10^{-4}	7.945×10^{-4}
0.15	1.769×10^{-3}	1.771×10^{-3}	1.792×10^{-3}	1.794×10^{-3}	1.800×10^{-3}	1.801×10^{-3}
0.20	3.179×10^{-3}	3.183×10^{-3}	3.221×10^{-3}	3.224×10^{-3}	3.236×10^{-3}	3.238×10^{-3}
0.25	5.039×10^{-3}	5.045×10^{-3}	5.105×10^{-3}	5.110×10^{-3}	5.129×10^{-3}	5.132×10^{-3}
0.30	7.388×10^{-3}	7.396×10^{-3}	7.484×10^{-3}	7.492×10^{-3}	7.519×10^{-3}	7.523×10^{-3}
0.35	1.028×10^{-2}	1.029×10^{-2}	1.041×10^{-2}	1.042×10^{-2}	1.046×10^{-2}	1.046×10^{-2}
0.40	1.378×10^{-2}	1.379×10^{-2}	1.395×10^{-2}	1.397×10^{-2}	1.402×10^{-2}	1.403×10^{-2}
0.45	1.798×10^{-2}	1.800×10^{-2}	1.821×10^{-2}	1.823×10^{-2}	1.830×10^{-2}	1.831×10^{-2}
0.50	2.301×10^{-2}	2.304×10^{-2}	2.330×10^{-2}	2.333×10^{-2}	2.341×10^{-2}	2.343×10^{-2}
0.55	2.904×10^{-2}	2.907×10^{-2}	2.941×10^{-2}	2.944×10^{-2}	2.954×10^{-2}	2.956×10^{-2}
0.60	3.630×10^{-2}	3.634×10^{-2}	3.676×10^{-2}	3.679×10^{-2}	3.692×10^{-2}	3.694×10^{-2}
0.65	4.514×10^{-2}	4.518×10^{-2}	4.569×10^{-2}	4.574×10^{-2}	4.590×10^{-2}	4.592×10^{-2}
0.70	5.605×10^{-2}	5.611×10^{-2}	5.673×10^{-2}	5.678×10^{-2}	5.698×10^{-2}	5.701×10^{-2}
0.75	6.984×10^{-2}	6.991×10^{-2}	7.066×10^{-2}	7.072×10^{-2}	7.096×10^{-2}	7.099×10^{-2}
0.80	8.783×10^{-2}	8.792×10^{-2}	8.882×10^{-2}	8.890×10^{-2}	8.918×10^{-2}	8.922×10^{-2}
0.85	1.125×10^{-1}	1.126×10^{-1}	1.137×10^{-1}	1.138×10^{-1}	1.141×10^{-1}	1.141×10^{-1}
0.90	1.490×10^{-1}	1.492×10^{-1}	1.504×10^{-1}	1.505×10^{-1}	1.509×10^{-1}	1.509×10^{-1}
0.95	2.121×10^{-1}	2.122×10^{-1}	2.135×10^{-1}	2.136×10^{-1}	2.140×10^{-1}	2.140×10^{-1}
0.99	3.362×10^{-1}	3.363×10^{-1}	3.373×10^{-1}	3.374×10^{-1}	3.377×10^{-1}	3.378×10^{-1}

TABLE 3

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled OH(I)-A(II) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{HPO_4}}$ = 6.000	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_4}}$ = 2.977	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{CO_3}}$ = 2.920	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{WO_4}}$ = 2.869	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{C_2O_4}}$ = 2.770	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SeO_4}}$ = 2.615
0.01	1.856×10^{-5}	1.405×10^{-5}	1.395×10^{-5}	1.386×10^{-5}	1.369×10^{-5}	1.342×10^{-5}
0.05	4.646×10^{-4}	3.516×10^{-4}	3.492×10^{-4}	3.417×10^{-4}	3.427×10^{-4}	3.359×10^{-4}
0.10	1.867×10^{-3}	1.413×10^{-3}	1.403×10^{-3}	1.394×10^{-3}	1.377×10^{-3}	1.350×10^{-3}
0.15	4.232×10^{-3}	3.202×10^{-3}	3.180×10^{-3}	3.160×10^{-3}	3.121×10^{-3}	3.059×10^{-3}
0.20	7.604×10^{-3}	5.752×10^{-3}	5.712×10^{-3}	5.677×10^{-3}	5.606×10^{-3}	5.495×10^{-3}
0.25	1.205×10^{-2}	9.111×10^{-3}	9.048×10^{-3}	8.991×10^{-3}	8.880×10^{-3}	8.704×10^{-3}
0.30	1.765×10^{-2}	1.334×10^{-2}	1.325×10^{-2}	1.317×10^{-2}	1.301×10^{-2}	1.275×10^{-2}
0.35	2.453×10^{-2}	1.854×10^{-2}	1.841×10^{-2}	1.830×10^{-2}	1.807×10^{-2}	1.771×10^{-2}
0.40	3.283×10^{-2}	2.481×10^{-2}	2.464×10^{-2}	2.449×10^{-2}	2.418×10^{-2}	2.370×10^{-2}
0.45	4.276×10^{-2}	3.231×10^{-2}	3.209×10^{-2}	3.189×10^{-2}	3.149×10^{-2}	3.087×10^{-2}
0.50	5.458×10^{-2}	4.124×10^{-2}	4.095×10^{-2}	4.069×10^{-2}	4.019×10^{-2}	3.940×10^{-2}
0.55	6.862×10^{-2}	5.184×10^{-2}	5.149×10^{-2}	5.116×10^{-2}	5.054×10^{-2}	4.954×10^{-2}
0.60	8.531×10^{-2}	6.448×10^{-2}	6.404×10^{-2}	6.364×10^{-2}	6.286×10^{-2}	6.163×10^{-2}
0.65	1.053×10^{-1}	7.964×10^{-2}	7.909×10^{-2}	7.860×10^{-2}	7.765×10^{-2}	7.613×10^{-2}
0.70	1.293×10^{-1}	9.797×10^{-2}	9.731×10^{-2}	9.671×10^{-2}	9.555×10^{-2}	9.370×10^{-2}
0.75	1.585×10^{-1}	1.205×10^{-1}	1.197×10^{-1}	1.189×10^{-1}	1.175×10^{-1}	1.153×10^{-1}
0.80	1.947×10^{-1}	1.487×10^{-1}	1.477×10^{-1}	1.468×10^{-1}	1.491×10^{-1}	1.424×10^{-1}
0.85	2.406×10^{-1}	1.851×10^{-1}	1.839×10^{-1}	1.829×10^{-1}	1.808×10^{-1}	1.776×10^{-1}
0.90	3.019×10^{-1}	2.348×10^{-1}	2.334×10^{-1}	2.322×10^{-1}	2.297×10^{-1}	2.258×10^{-1}
0.95	3.941×10^{-1}	3.119×10^{-1}	3.102×10^{-1}	3.086×10^{-1}	3.056×10^{-1}	3.009×10^{-1}
0.99	5.562×10^{-1}	4.512×10^{-1}	4.490×10^{-1}	4.471×10^{-1}	4.433×10^{-1}	4.373×10^{-1}

(Table 3 continued)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{CrO_4}}$ = 2.500	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SO_3}}$ = 2.478	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SO_4}}$ = 2.475	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_3}}$ = 2.329	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_8}}$ = 2.302	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_6}}$ = 2.129
0.01	1.321×10^{-5}	1.317×10^{-5}	1.317×10^{-5}	1.290×10^{-5}	1.285×10^{-5}	1.253×10^{-5}
0.05	3.308×10^{-4}	3.298×10^{-4}	3.296×10^{-4}	3.230×10^{-4}	3.217×10^{-4}	3.136×10^{-4}
0.10	1.329×10^{-3}	1.324×10^{-3}	1.324×10^{-3}	1.298×10^{-3}	1.293×10^{-3}	1.260×10^{-3}
0.15	3.012×10^{-3}	3.002×10^{-3}	3.002×10^{-3}	2.941×10^{-3}	2.930×10^{-3}	2.856×10^{-3}
0.20	5.411×10^{-3}	5.395×10^{-3}	5.393×10^{-3}	5.264×10^{-3}	5.263×10^{-3}	5.131×10^{-3}
0.25	8.571×10^{-3}	8.545×10^{-3}	8.541×10^{-3}	8.369×10^{-3}	8.337×10^{-3}	8.127×10^{-3}
0.30	1.255×10^{-2}	1.252×10^{-2}	1.251×10^{-2}	1.226×10^{-2}	1.221×10^{-2}	1.190×10^{-2}
0.35	1.744×10^{-2}	1.739×10^{-2}	1.738×10^{-2}	1.703×10^{-2}	1.697×10^{-2}	1.654×10^{-2}
0.40	2.334×10^{-2}	2.327×10^{-2}	2.326×10^{-2}	2.279×10^{-2}	2.271×10^{-2}	2.214×10^{-2}
0.45	3.040×10^{-2}	3.031×10^{-2}	3.030×10^{-2}	2.969×10^{-2}	2.957×10^{-2}	2.883×10^{-2}
0.50	3.880×10^{-2}	3.868×10^{-2}	3.867×10^{-2}	3.789×10^{-2}	3.775×10^{-2}	3.680×10^{-2}
0.55	4.879×10^{-2}	4.864×10^{-2}	4.862×10^{-2}	4.765×10^{-2}	4.747×10^{-2}	4.629×10^{-2}
0.60	6.070×10^{-2}	6.052×10^{-2}	6.049×10^{-2}	5.929×10^{-2}	5.906×10^{-2}	5.760×10^{-2}
0.65	7.499×10^{-2}	7.477×10^{-2}	7.474×10^{-2}	7.326×10^{-2}	7.298×10^{-2}	7.119×10^{-2}
0.70	9.230×10^{-2}	9.204×10^{-2}	9.200×10^{-2}	9.020×10^{-2}	8.986×10^{-2}	8.768×10^{-2}
0.75	1.136×10^{-1}	1.133×10^{-1}	1.132×10^{-1}	1.111×10^{-1}	1.106×10^{-1}	1.080×10^{-1}
0.80	1.404×10^{-1}	1.400×10^{-1}	1.399×10^{-1}	1.373×10^{-1}	1.368×10^{-1}	1.338×10^{-1}
0.85	1.791×10^{-1}	1.746×10^{-1}	1.746×10^{-1}	1.714×10^{-1}	1.708×10^{-1}	1.670×10^{-1}
0.90	2.228×10^{-1}	2.223×10^{-1}	2.222×10^{-1}	2.184×10^{-1}	2.177×10^{-1}	2.132×10^{-1}
0.95	2.973×10^{-1}	2.966×10^{-1}	2.965×10^{-1}	2.920×10^{-1}	2.911×10^{-1}	2.857×10^{-1}
0.99	4.328×10^{-1}	4.320×10^{-1}	4.319×10^{-1}	4.262×10^{-1}	4.251×10^{-1}	4.184×10^{-1}

TABLE 4

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled A(II)-OH(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{HPO_4}}{\bar{D}_{OH}}$ = 0.170	$\alpha = \frac{\bar{D}_{S_2O_4}}{\bar{D}_{OH}}$ = 0.336	$\alpha = \frac{\bar{D}_{CO_3}}{\bar{D}_{OH}}$ = 0.340	$\alpha = \frac{\bar{D}_{WO_4}}{\bar{D}_{OH}}$ = 0.348	$\alpha = \frac{\bar{D}_{C_2O_4}}{\bar{D}_{OH}}$ = 0.360	$\alpha = \frac{\bar{D}_{SeO_4}}{\bar{D}_{OH}}$ = 0.382
0.01	4.982×10^{-6}	6.126×10^{-6}	6.152×10^{-6}	6.205×10^{-6}	6.283×10^{-6}	6.426×10^{-6}
0.05	1.248×10^{-4}	1.534×10^{-4}	1.541×10^{-4}	1.554×10^{-4}	1.573×10^{-4}	1.609×10^{-4}
0.10	5.027×10^{-4}	6.170×10^{-4}	6.197×10^{-4}	6.202×10^{-4}	6.328×10^{-4}	6.472×10^{-4}
0.15	1.144×10^{-3}	1.402×10^{-3}	1.408×10^{-3}	1.419×10^{-3}	1.437×10^{-3}	1.469×10^{-3}
0.20	2.068×10^{-3}	2.526×10^{-3}	2.536×10^{-3}	2.557×10^{-3}	2.589×10^{-3}	2.646×10^{-3}
0.25	3.302×10^{-3}	4.016×10^{-3}	4.033×10^{-3}	4.066×10^{-3}	4.116×10^{-3}	4.206×10^{-3}
0.30	4.886×10^{-3}	5.912×10^{-3}	5.936×10^{-3}	5.984×10^{-3}	6.056×10^{-3}	6.186×10^{-3}
0.35	6.875×10^{-3}	8.266×10^{-3}	8.298×10^{-3}	8.363×10^{-3}	8.461×10^{-3}	8.639×10^{-3}
0.40	9.341×10^{-3}	1.115×10^{-2}	1.119×10^{-2}	1.127×10^{-2}	1.140×10^{-2}	1.163×10^{-2}
0.45	1.238×10^{-2}	1.464×10^{-2}	1.470×10^{-2}	1.481×10^{-2}	1.497×10^{-2}	1.526×10^{-2}
0.50	1.614×10^{-2}	1.888×10^{-2}	1.895×10^{-2}	1.908×10^{-2}	1.928×10^{-2}	1.965×10^{-2}
0.55	2.077×10^{-2}	2.403×10^{-2}	2.411×10^{-2}	2.407×10^{-2}	2.451×10^{-2}	2.496×10^{-2}
0.60	2.648×10^{-2}	3.030×10^{-2}	3.040×10^{-2}	3.059×10^{-2}	3.088×10^{-2}	3.141×10^{-2}
0.65	3.347×10^{-2}	3.799×10^{-2}	3.810×10^{-2}	3.832×10^{-2}	3.866×10^{-2}	3.930×10^{-2}
0.70	4.332×10^{-2}	5.000×10^{-2}	5.015×10^{-2}	5.045×10^{-2}	5.090×10^{-2}	5.172×10^{-2}
0.75	5.437×10^{-2}	6.245×10^{-2}	6.264×10^{-2}	6.301×10^{-2}	6.335×10^{-2}	6.555×10^{-2}
0.80	6.915×10^{-2}	7.887×10^{-2}	7.909×10^{-2}	7.954×10^{-2}	8.020×10^{-2}	8.141×10^{-2}
0.85	9.021×10^{-2}	1.017×10^{-1}	1.020×10^{-1}	1.025×10^{-1}	1.033×10^{-1}	1.048×10^{-1}
0.90	1.236×10^{-1}	1.366×10^{-1}	1.369×10^{-1}	1.376×10^{-1}	1.385×10^{-1}	1.402×10^{-1}
0.95	1.890×10^{-1}	2.001×10^{-1}	2.005×10^{-1}	2.011×10^{-1}	2.020×10^{-1}	2.038×10^{-1}
0.99	3.327×10^{-1}	3.337×10^{-1}	3.338×10^{-1}	3.342×10^{-1}	3.348×10^{-1}	3.359×10^{-1}

(Table 4 continued)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ				
	$\alpha = \frac{\bar{D}_{CrO_4}}{\bar{D}_{OH}}$ = 0.400	$\alpha = \frac{\bar{D}_{SO_3/SO_4}}{\bar{D}_{OH}}$ = 0.404	$\alpha = \frac{\bar{D}_{S_2O_3}}{\bar{D}_{OH}}$ = 0.429	$\alpha = \frac{\bar{D}_{S_2O_8}}{\bar{D}_{OH}}$ = 0.434	$\alpha = \frac{\bar{D}_{S_2O_6}}{\bar{D}_{OH}}$ = 0.469
0.01	6.543×10^{-6}	6.568×10^{-6}	6.729×10^{-6}	6.760×10^{-6}	6.982×10^{-6}
0.05	1.638×10^{-4}	1.645×10^{-4}	1.685×10^{-4}	1.693×10^{-4}	1.748×10^{-4}
0.10	6.588×10^{-4}	6.614×10^{-4}	6.774×10^{-4}	6.806×10^{-4}	7.028×10^{-4}
0.15	1.496×10^{-3}	1.502×10^{-3}	1.538×10^{-3}	1.545×10^{-3}	1.595×10^{-3}
0.20	2.693×10^{-3}	2.702×10^{-3}	2.768×10^{-3}	2.781×10^{-3}	2.871×10^{-3}
0.25	4.279×10^{-3}	4.296×10^{-3}	4.397×10^{-3}	4.417×10^{-3}	4.558×10^{-3}
0.30	6.292×10^{-3}	6.316×10^{-3}	6.462×10^{-3}	6.492×10^{-3}	6.695×10^{-3}
0.35	8.784×10^{-3}	8.817×10^{-3}	9.017×10^{-3}	9.057×10^{-3}	9.337×10^{-3}
0.40	1.182×10^{-2}	1.187×10^{-2}	1.213×10^{-2}	1.218×10^{-2}	1.255×10^{-2}
0.45	1.551×10^{-2}	1.556×10^{-2}	1.590×10^{-2}	1.596×10^{-2}	1.643×10^{-2}
0.50	1.995×10^{-2}	2.002×10^{-2}	2.044×10^{-2}	2.052×10^{-2}	2.111×10^{-2}
0.55	2.532×10^{-2}	2.541×10^{-2}	2.592×10^{-2}	2.602×10^{-2}	2.674×10^{-2}
0.60	3.185×10^{-2}	3.194×10^{-2}	3.256×10^{-2}	3.268×10^{-2}	3.355×10^{-2}
0.65	3.982×10^{-2}	3.993×10^{-2}	4.302×10^{-2}	4.316×10^{-2}	4.419×10^{-2}
0.70	5.238×10^{-2}	5.233×10^{-2}	5.344×10^{-2}	5.362×10^{-2}	5.488×10^{-2}
0.75	6.536×10^{-2}	6.554×10^{-2}	6.664×10^{-2}	6.686×10^{-2}	6.839×10^{-2}
0.80	8.238×10^{-2}	8.260×10^{-2}	8.394×10^{-2}	8.421×10^{-2}	8.606×10^{-2}
0.85	1.060×10^{-1}	1.062×10^{-1}	1.078×10^{-1}	1.082×10^{-1}	1.104×10^{-1}
0.90	1.416×10^{-1}	1.419×10^{-1}	1.438×10^{-1}	1.442×10^{-1}	1.468×10^{-1}
0.95	2.053×10^{-1}	2.056×10^{-1}	2.076×10^{-1}	2.080×10^{-1}	2.109×10^{-1}
0.99	3.369×10^{-1}	3.372×10^{-1}	3.387×10^{-1}	3.390×10^{-1}	3.413×10^{-1}

CHAPTER - 4

ION EXCHANGE AND ADSORPTION EQUILIBRIA ON SOME SYNTHETIC INORGANIC ION EXCHANGERS

Acta Chimica Hungarica 115 (4), pp. 403–413 (1984)

4.1

THERMODYNAMICS OF Ca^{2+}–H^+ AND Mg^{2+}–H^+ EXCHANGES ON ANTIMONY(V) SILICATE CATION EXCHANGER

K. G. VARSHNEY*, R. P. SINGH** and S. RANI

(Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh-202001, India)

Received February 16, 1983
In revised form May 17, 1983
Accepted for publication June 7, 1983

The equilibrium exchange of Ca^{2+} and Mg^{2+} ions with the hydrogen form of antimony(V) silicate has been studied at 25 and 50 °C and the various thermodynamic parameters have been evaluated. The activity coefficients have also been calculated which give the excess free energies (ΔG^x_m), enthalpies (ΔH^x_m) and entropies (ΔS^x_m) of mixing. On the basis of these results an attempt has been made to correlate the ion-exchange phenomenon with the various thermodynamic data.

Introduction

Inorganic ion exchangers have received sufficient attention in separating of metal ions. Although a large number of such materials have been synthesized [1], only a few of them have been studied thermodynamically [2–7]. Also a detailed and systematic thermodynamic approach is lacking for their ion-exchange behaviour. Antimony(V) silicate was prepared in these laboratories as a crystalline material with an excellent ion-exchange property [8]. The present article summarized its detailed and systematic thermodynamic study for the Ca^{2+} and Mg^{2+} exchanges with H^+ ions.

Experimental

Reagents

Antimony(V) chloride used in this study was a product of Koch-Light Laboratories Ltd. (Colnbrook Bucks England) and sodium silicate was a Reidal (DEHAENAG, Seelze Hannover) product. Other reagents and chemicals were either of BDH or AnalaR grade.

Apparatus

A water-bath incubator shaker was used in the equilibrium studies. Its temperature was adjusted within ±0.5 °C.

* To whom correspondence should be addressed.
** Section of Plant Pathology and Nematology, Department of Botany, Aligarh Muslim University, Aligarh.

Preparation of the reagent solutions

0.1 *M* solutions of antimony(V) chloride and sodium silicate were prepared in 1 *M* HCl and demineralized water (DMW), respectively. The solutions of metals under study were prepared by dissolving their nitrates in DMW.

Synthesis of antimony(V) silicate (SbSi)

It was synthesized by the following method [8]:

0.1 *M* solution of antimony(V) chloride and sodium silicate were mixed under constant stirring in a volume ratio of 2 : 1 and the pH of the resultant gel was adjusted to ~1 by adding sodium hydroxide. After 24 hrs the gel was filtered and washed with DMW and then dried in an air oven at 45 °C. It was converted into small granules by putting in DMW and the granules were converted into the H^+-form by treating them with 1 *M* HNO_3 for 24 hrs with occasional shaking and intermittently replacing the acid. After washing the excess acid the granules were dried at 45 °C which had ion-exchange capacity for Ca^{2+} 1.1 and for Mg^{2+} 1.53 meq/dry g, respectively, determined by the usual column process.

Equilibrium experiment

0.2 g fractions of the exchanger in H^+-form were shaken in various stoppered conical flasks at the desired temperatures (25° and 50° C), for 3 hours with the metal ion solutions (20 mL) with a constant ionic strength (0.03 *M*) adjusted by adding the appropriate amounts of HNO_3. The supernatant solution was analysed for the metal and hydrogen ions by EDTA and NaOH titrations, respectively.

Results and Discussion

As shown on Fig. 1 the exchange equilibrium on antimony(V) silicate has been attained within 3 hours and hence this period was chosen in all the equilibrium studies. The interaction in the system may be described as follows:

$$\bar{C}_H + C_M \rightleftharpoons \bar{C}_M + C_H \qquad (1)$$

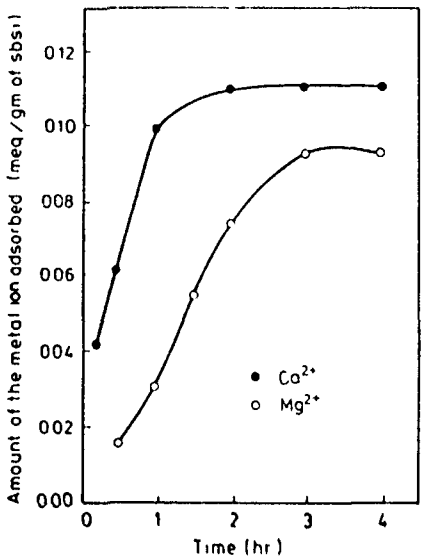


Fig. 1. Plots of amount adsorbed of Ca^{2+} and Mg^{2+} versus time on antimony(V) silicate

where bar represents the equivalent concentration of the ion concerned in the exchanger phase and the rest in the solution phase. M represents the metal ion (Ca^{2+} or Mg^{2+}). The equivalent ionic fractions (X_M and X_H) of the counter ions in SbSi and the corresponding values in solution (X_M and X_H) were calculated by the expressions:

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}}, \quad X_M = \frac{C_M}{C}, \quad \bar{X}_H = \frac{\bar{C}_H}{\bar{C}}, \quad X_H = \frac{C_H}{C}$$

where $\bar{C}$ and C are the total electrolyte concentrations in the solid and solution phases, respectively.

To examine the affinity for the interacting ions, the separation factors and selectivity coefficients were calculated by the following expressions, assuming the ratio of the activity coefficients in solution to be unity [9, 10]. Under these conditions K_c ceases to express interactions in solutions.

$$\alpha_H^M = \frac{\bar{X}_M}{\bar{X}_H} \cdot \frac{X_H}{X_M} \tag{2}$$

and

$$K_c = \frac{\bar{X}_M}{[\bar{X}_H]^2} \cdot \frac{[X_H]^2}{X_M} \tag{3}$$

The various values obtained at 25 and 50 °C are summarized in Tables I and II and the exchange isotherms are shown in Fig. 2. As it is clear from this figure the Ca^{2+} ions are preferably adsorbed by the SbSi phase at all concentrations, the preference being higher at 50 °C. However, in case of the Mg^{2+}— H^+ exchange the reverse is true i.e. the material has a preference for H^+ ions at both temperatures over the entire concentration range studied. This conclu-

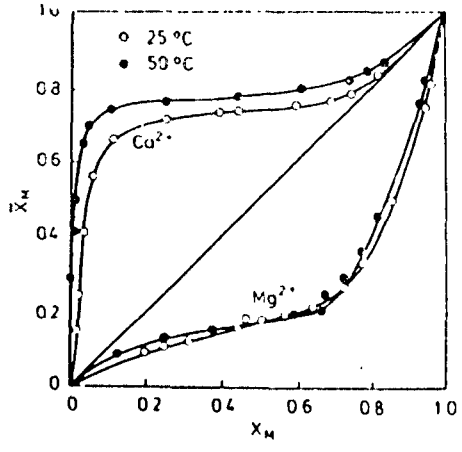


Fig. 2. Exchange isotherms of Ca^{2+} H^+ and Mg^{2+} H^+ exchanges on antimony(V) silicate at 25 and 50 °C

Table I

Values of the equivalent ionic fractions of calcium and hydrogen, separation factors and selectivity quotients at 25 and 50 °C for the Ca^{2+}—H^+ exchange on antimony (V) silicate

Sl. No.	$\bar{X}_{Ca}$	X_{Ca}	$\bar{X}_H$	X_H	α_H^{Ca}	K_c	log K_c
				At 25 °C			
1.	0.15	0.02	0.71	0.94	13.34	17.68	1.25
2.	0.25	0.03	0.64	0.94	14.84	21.85	1.34
3.	0.41	0.04	0.48	0.87	21.28	38.57	1.59
4.	0.55	0.06	0.39	0.79	19.93	40.37	1.61
5.	0.67	0.13	0.38	0.75	10.60	21.14	1.33
6.	0.72	0.25	0.35	0.71	5.77	11.70	1.07
7.	0.74	0.35	0.32	0.66	4.41	9.25	0.97
8.	0.74	0.45	0.29	0.66	3.81	8.81	0.95
9.	0.75	0.60	0.26	0.51	2.42	4.70	0.67
10.	0.76	0.70	0.23	0.13	0.62	0.36	− 0.44
11.	0.79	0.75	0.23	0.13	0.61	0.35	−0.45
12.	0.84	0.82	0.17	0.13	0.77	0.59	− 0.23
				At 50 °C			
1.	0.29	0.01	0.71	0.99	40.93	57.46	1.76
2.	0.42	0.01	0.58	0.99	71.14	121.35	2.08
3.	0.50	0.02	0.44	0.99	55.48	124.01	2.04
4.	0.66	0.04	0.41	0.98	45.26	109.36	2.03
5.	0.70	0.05	0.30	0.95	45.19	145.09	2.16
6.	0.74	0.11	0.26	0.89	22.58	76.12	1.88
7.	0.77	0.26	0.24	0.81	10.23	35.40	1.55
8.	0.78	0.45	0.22	0.74	5.95	20.29	1.31
9.	0.80	0.62	0.20	0.66	4.16	13.47	1.13
10.	0.82	0.74	0.16	0.18	1.24	1.38	0.14
11.	0.84	0.80	0.13	0.16	1.35	1.86	0.27
12.	0.86	0.84	0.08	0.15	1.83	3.27	0.51

sion is substantiated by the values of the separation factors and selectivity coefficients (Fig. 3).

The thermodynamic equilibrium constants were obtained [11] from the relationship:

$$\ln K = (Z_A - Z_B) + \int_0^1 \ln K_C \, dX_M \qquad (1)$$

Table II

Values of the equivalent ionic fractions of magnesium and hydrogen, separation factors and selectivity quotients at 25 and 50 °C for the $Mg^{2+}-H^+$ exchange on antimony(V) silicate

Sl. No.	$\bar{X}_{Mg}$	X_{Mg}	$\bar{X}_H$	X_H	α_H^{Mg}	K_c	log K_c
				At 25 °C			
1.	0.10	0.20	0.88	0.43	0.25	0.12	−0.91
2.	0.12	0.25	0.84	0.31	0.18	0.07	1.17
3.	0.13	0.32	0.83	0.27	0.13	0.04	−1.36
4.	0.17	0.45	0.80	0.24	0.11	0.03	1.46
5.	0.19	0.46	0.78	0.22	0.12	0.03	1.50
6.	0.20	0.57	0.76	0.19	0.09	0.02	−1.68
7.	0.22	0.65	0.76	0.17	0.08	0.02	−1.75
8.	0.27	0.73	0.74	0.05	0.03	0.00	−2.78
9.	0.34	0.78	0.72	0.05	0.03	0.00	−2.68
10.	0.50	0.85	0.50	0.05	0.06	0.01	−2.28
11.	0.74	0.95	0.26	0.03	0.09	0.01	−2.00
12.	0.81	0.97	0.19	0.03	0.12	0.02	−1.70
				At 50 °C			
1.	0.09	0.13	0.86	0.49	0.41	0.23	−0.64
2.	0.14	0.25	0.84	0.41	0.26	0.13	−0.90
3.	0.17	0.38	0.83	0.31	0.16	0.06	−1.23
4.	0.18	0.51	0.82	0.28	0.12	0.04	−1.40
5.	0.20	0.59	0.81	0.25	0.10	0.03	−1.50
6.	0.21	0.66	0.80	0.22	0.09	0.02	−1.61
7.	0.25	0.69	0.80	0.20	0.09	0.02	−1.65
8.	0.29	0.73	0.75	0.06	0.03	0.00	−2.62
9.	0.35	0.78	0.71	0.05	0.03	0.00	−2.57
10.	0.45	0.82	0.68	0.05	0.04	0.00	−2.47
11.	0.76	0.95	0.24	0.03	0.11	0.01	−1.84
12.	0.82	0.97	0.18	0.03	0.15	0.03	−1.59

where Z_A and Z_B are the valencies of the competing ions. The integrals were evaluated from the areas under the curves of Fig. 3 using the trapezoidal rule [12] and the K values are given in Table III. Since the K values are higher at 50 °C than at 25 °C the affinity of SbSi is higher at the former temperature. Also, a higher K value for the Ca^{2+}—H^+ exchange as compared to the Mg^{2+}—H^+ exchange points to a higher affinity for the Ca^{2+} ions.

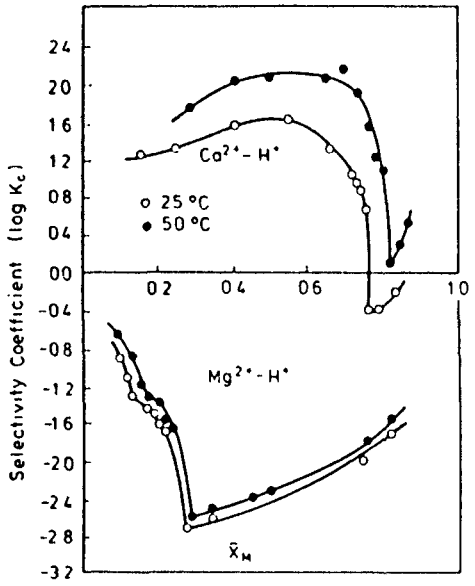


Fig. 3. Plots of log K_c versus $\bar{X}_M$ on antimony(V) silicate for Ca^{2+} - H^+ and Mg^+ exchanges at 25 and 50 °C

Table III

Thermodynamic values of the Ca^{2+} H^+ *and* Mg^{2+} H^+ *exchanges at 25 and 50 °C on antimony(V) silicate*

Thermodynamic parameters	Values for the Ca^{2+}—H^+ system at		Values for the Mg^{2+} - H^+ system at	
	25 °C	50 °C	25 °C	50 °C
K	18.33	25.96	0.07	0.12
$\Delta G°$ (kJ mol^{-1})	−7.22	−8.76	6.70	5.63
$\Delta H°$ (kJ mol^{-1})	11.13		19.45	
$\Delta S°$ (Jmol^{-1} k^{-1})	60	60	40	40

The standard free energies of exchange ($\Delta G°$) for the interaction (1) were calculated [13] from the relationship:

$$\Delta G° = -RT \ln K \tag{5}$$

where R is the universal gas constant and T is the temperature in Kelvin.

The standard enthalpy changes ($\Delta H°$) were then calculated from the Van't Hoff isochore:

$$\ln \left(\frac{K_{T_2}}{K_{T_1}}\right) = - \frac{\Delta H°}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{6}$$

and standard entropy changes ($\Delta S°$) by the equation:

$$\Delta G° = \Delta H° - T\Delta S° \tag{7}$$

Table III also summarized these values. The negative standard free energy change ($\Delta G°$) for the Ca^{2+}—H^+ interaction means that Ca^{2+} is preferably adsorbed on SbSi as compared to the H^+ ions and the preference increases at a higher temperature. Similarly, a positive value of $\Delta G°$ for the Mg^{2+}—H^+ interaction at both temperatures indicates that SbSi had a lower preference for Mg^{2+} than for H^+ at both temperatures. The exchange process is probably endothermic as the positive enthalpy changes indicate. It is supported by the experimental observations as the adsorption is higher at a higher temperature. Positive values of standard entropy change suggest that the metal ions are less strongly bound to the exchanger than the H^+ ions.

The activity coefficients of M^{2+} and H^+ ions were calculated [14, 15] from the following expressions:

$$\ln f_M = (\bar{X}_M - 1) \ln K_c - \int_0^{\bar{X}_M} \ln K_c \, d\bar{X}_M \tag{8}$$

$$\ln f_H = \bar{X}_M \ln K_c - \int_0^{\bar{X}_M} \ln K_c \, d\bar{X}_M \tag{9}$$

the values thus obtained are given in Table IV.

In the Ca^{2+}—H^+ exchange the f_M values are less than unity at both temperatures. However, in the Mg^{2+}—H^+ exchange the values are greater than unity and generally increase with an increase in the $\bar{X}_{Mg}$ values indicating a high order heterogeneity in the distribution of ions at the exchanger surface. In this respect our material behaves in a manner similar to the others reported earlier [16, 17]. Soils also behave similarly [18].

To further examine the deviation of these heterogeneous systems from ideality, the excess thermodynamic functions for these systems were calculated [19, 20] from the expressions:

$$\Delta G_m^x = RT[\bar{X}_M \ln f_M + \bar{X}_H \ln f_H]$$

$$\Delta H_m^x = -RT^2\left[\bar{X}_M\left(\frac{\partial \ln f_M}{\partial T}\right) + \bar{X}_H\left(\frac{\partial \ln f_H}{\partial T}\right)\right] \tag{11}$$

and

$$\Delta G_m^x = \Delta H_m^x - T\Delta S_m^x \tag{12}$$

where ΔG_m^x, ΔH_m^x and ΔS_m^x are the excess free energies, enthalpies and entropies of mixing.

The values of the excess thermodynamic functions are markedly different (Tables V and VI). Also the excess free energy change is negative for the

Table IV

Activity coefficients for the different Ca^{2+} H^+ *and* Mg^{2+} H^+ *compositions on antimony(V) silicate at 25 and 50 °C*

Sl. No.	Values at 25 °C			Values at 50 °C		
	$\bar{X}_{Ca}$	f_{Ca}	f_H	$\bar{X}_{Ca}$	f_{Ca}	f_H
			Ca^{2+}—H^+			
1.	0.15	0.09	1.52	0.29	0.06	3.19
2.	0.25	0.07	1.62	0.42	0.03	4.16
3.	0.41	0.05	1.95	0.50	0.03	3.27
4.	0.55	0.01	2.00	0.66	0.04	4.07
5.	0.67	0.06	1.36	0.70	0.04	5.40
6.	0.72	0.08	0.89	0.74	0.04	3.18
7.	0.74	0.08	0.76	0.77	0.05	1.88
8.	0.74	0.08	0.73	0.78	0.06	1.00
9.	0.75	0.10	0.45	0.80	0.07	0.88
10.	0.76	0.18	0.07	0.82	0.10	0.14
11.	0.79	0.18	0.22	0.84	0.10	0.18
12.	0.84	0.16	0.10	0.86	0.09	0.29
			Mg^{2+}—H^+			
1.	0.10	6.65	0.82	0.09	3.87	0.88
2.	0.12	11.05	0.75	0.14	6.18	0.78
3.	0.13	16.39	0.71	0.16	11.06	0.65
4.	0.17	19.95	0.68	0.18	11.66	0.69
5.	0.19	20.62	0.66	0.20	19.84	0.63
6.	0.20	29.09	0.61	0.21	25.43	0.62
7.	0.22	32.75	0.58	0.25	23.72	0.53
8.	0.27	208.90	0.35	0.29	137.20	0.33
9.	0.34	177.30	0.39	0.35	142.10	0.38
10.	0.50	117.00	0.61	0.45	104.20	0.36
11.	0.74	94.32	0.94	0.76	49.58	0.71
12.	0.81	86.62	1.56	0.82	42.39	1.10

Ca^{2+}—H^+ exchange and increases with the increase in the equivalent ionic fraction of the Ca^{2+} ions in the SbSi phase. However, in case of the Mg^{2+}—H^+ exchange this value is positive and increases with an increase in Mg^{2+} ion concentration. It appears therefore that a heterogeneous mixture of H^+ and Ca^{2+} ions on the SbSi surface is more stable than the pure homoionic form in the Ca^{2+}—H^+ exchange process. The reverse appears to be true for the Mg^{2+}—H^+ exchange.

Table V

The excess free energies, enthalpies and entropies of mixing, for the Ca^{2+}—H^+ exchange on antimony(V) silicate at 25 and 50 °C

Sl. No.	$\bar{X}_{Ca}$	ΔG_m^E (kJ mol^{-1})	ΔH_m^E (kJ mol^{-1})	ΔS_m^E (J · mol^{-1} k^{-1})
		At 25 °C		
1.	0.15	−0.18	−13.67	−50
2.	0.25	−0.87	−12.08	−40
3.	0.41	−2.26	0.64	10
4.	0.55	−5.63	−29.62	−80
5.	0.67	−4.25	− 4.63	0
6.	0.72	−4.71	− 0.27	20
7.	0.74	−4.78	0.96	20
8.	0.74	−4.83	3.67	30
9.	0.75	−4.87	3.67	30
10.	0.77	−3.58	7.81	40
11.	0.79	−4.17	16.17	70
12.	0.84	−4.77	15.01	70
		At 50 °C		
1.	0.29	−0.05	−13.82	−40
2.	0.42	−1.55	− 7.96	−20
3.	0.50	−3.46	3.33	−20
4.	0.66	−4.27	−39.95	−110
5.	0.71	−4.88	− 0.93	10
6.	0.74	−5.48	3.83	30
7.	0.77	−5.68	4.14	30
8.	0.78	−5.86	5.47	40
9.	0.80	−5.93	6.26	40
10.	0.82	−5.88	12.24	60
11.	0.84	−5.87	19.48	80
12.	0.86	−5.89	14.67	60

The enthalpies and entropies of mixing for the Ca^{2+}—H^+ exchange are negative upto a certain limit ($\bar{X}_{Ca}$ = 0.72 and 0.70 at 25 and 50 °C respectively). Thereafter, the values are positive. This reversal in the signs indicates a higher binding strength of the ion mixture as compared to a single ion. In case of the Mg^{2+}—H^+ exchange, however, no definite order is found. It is in accordance with the work of Howery and Thomas [15] for the ion-exchange process on the mineral clinoptilotite.

Table VI

The excess free energies, enthalpies and entropies of mixing for the $Mg^{2+}-H^+$ *exchange on antimony(V) silicate at* 25 *and* 50 °C

Sl. No.	$\bar{X}_{Mg}$	ΔG^E_m (kJ mole^{-1})	ΔH^E_m (kJ mol^{-1})	ΔS^E_m (J · mol^{-1} K^{-1})
		At 25 °C		
1.	0.10	0.04	3.50	10
2.	0.12	0.15	3.18	10
3.	0.13	0.22	0.58	0
4.	0.17	0.53	2.75	10
5.	0.19	0.62	−0.59	0
6.	0.20	0.73	1.34	0
7.	0.22	0.90	0.06	0
8.	0.27	1.64	2.10	0
9.	0.34	2.69	2.29	0
10.	0.50	5.30	−6.28	60
11.	0.74	8.31	11.87	10
12.	0.81	9.19	26.49	60
		At 50 °C		
1.	0.09	0.03	3.89	10
2.	0.14	0.12	3.97	10
3.	0.16	0.10	−0.29	0
4.	0.18	0.35	3.35	10
5.	0.20	0.61	−0.72	0
6.	0.21	0.81	1.66	0
7.	0.25	0.75	0.22	0
8.	0.29	1.63	2.75	0
9.	0.35	2.87	3.48	0
10.	0.45	3.76	14.52	40
11.	0.76	7.78	19.37	40
12.	0.82	8.30	22.53	40

The authors are grateful to Prof. M. Qureshi for providing research facilities and to the CSIR (India) for the financial support of one of them (S.R.).

REFERENCES

[1] Walton, H. F.: Anal. Chem., 52, 15R (1980)
[2] Larsen, E. M., Vissers, D. R.: J. Phys. Chem., 64, 1732 (1960)
[3] Baetsle, L. H.: J. Inorg. Nucl. Chem., 25, 271 (1963)
[4] Nancollas, G. H., Tilak, B. V. K. S. R. A.: J. Inorg. Nucl. Chem., 31, 3643 (1969)
[5] Alberti, G., Costantino, U.: J. Inorg. Nucl. Chem., 36, 653 (1974)

[6] Rawat, J. P., Singh, D. K.: Anal. Chim. Acta, **87**, 157 (1976)
[7] Rawat, J. P., Muktawat, K. P. S.: J. Inorg. Nucl. Chem., **43**, 2121 (1981)
[8] Varshney, K. G., Sharma, U., Rani, S., Premadas, A.: Sep. Sci. and Tech., **17**, 1527 (1982)
[9] Robinson, R. A., Strokes, R. H.: Electrolyte Solutions, Butterworths, London 1959
[10] Singhal, J. P., Singh, R. P.: J. Soil. Sci., **27**, 12 (1976)
[11] Gains, G. L., Thomas, H. C.: J. Chem. Phys., **21**, 714 (1953)
[12] Singhal, J. P., Singh, R. P.: Acta Chim. Acad. Sci. Hung., **93**, 307 (1977)
[13] Glasstone, S.: Text Book of Physical Chemistry, McMillan and Company Ltd, London 1960
[14] El-Sayed, M. H., Burau, R. G., Babcock, K. L.: Soil Sci. Soc. Amer. Proc., **34**, 397 (1970)
[15] Howery, D. G., Thomas, H. C.: J. Phys. Chem., **69**, 531 (1965)
[16] Singhal, J. P., Singh, R. P., Kumar, D.: J. Ind. Chem. Soc., **52**, 1015 (1975)
[17] Robinson, R. A., Strokes, R. H.: Trans. Faraday Soc., **45**, 612 (1949)
[18] Diest, J., Talibuddeen, O.: J. Soil Sci., **18**, 125 (1967)
[19] Gast, R. G., Klobe, W. D.: Clays and Clay Minerals, **19**, 311 (1971)
[20] Vanselow, A. P.: J. Soil Sci., **33**, 95 (1932)

© *Proc. Indian natn. Sci. Acad.*, 50, A, No. 1, 1984, pp. 75-84.
Printed in India.
Physical Chemistry

4.2 THERMODYNAMICS OF Ba^{2+}-H^+ AND Sr^{2+}-H^+ EXCHANGES ON ANTIMONY(V) SILICATE CATION EXCHANGER

K. G. VARSHNEY*, R P. SINGH† *and* SIMA RANI

Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology, Aligarh Muslim University, Aligarh-202 001, India

(*Received 1 June 1983; after revision 19 September 1983*)

The equilibrium exchange of Ba^{2+} and Sr^{2+} have been studied with the H^+ ions on antimony(V) silicate cation exchanger at 25° and 50°C. On the basis of the exchange isotherms, various thermodynamic parameters have been calculated and some predictions made for the exchange processes taking place in the material. The activity coefficients have also been evaluated which give the excess free energies (ΔG^E_m), enthalpies (ΔH^E_m) and entropies (ΔS^E_m) of mixing.

Key Words : Thermodynamics; Cation Exchange; Antimony(V) Silicate

INTRODUCTION

INORGANIC materials possessing ion-exchange properties are well known for their metal-ion selectivity (Walton, 1980). However, only a few of them have been studied thoroughly to evaluate their ion-exchange behaviour on the basis of a fundamental approach such as thermodynamics (Larsen & Vissers, 1960; Baetsle, 1963; Nancollas, & Tilak, 1969; Alberti & Costantino, 1974; Rawat & Thind, 1980; and Rawat & Muktawat, 1981). Antimony(V) silicate was prepared in these laboratories, as a crystalline material with an excellent reproducibility in its cation exchange behaviour (Varshney *et al.*, 1982). Present article, therefore, summarizes our efforts to have a thermodynamic study for the exchange of Ba^{2+} and Sr^{2+} ions with H^+ ions on this material.

EXPERIMENTAL

Reagents

Antimony(V) chloride used in this study was a product of Kochlight Laboratories Ltd. (Colnbrook Bucks England, Hanover) product. Other reagents and chemicals were either of BDH or AnalaR grade.

*Author for correspondence.

†Section of Plant Pathology and Nematology, Department of Botany, Aligarh Muslim University, Aligarh.

Apparatus

A water bath incubator shaker having a temperature variation of ± 0.5°C was used for all the equilibrium studies.

Synthesis of Antimony (V) Silicate

A decimolar solution of antimony(V) chloride in 4M HCl was mixed with a decimolar solution of sodium silicate in demineralized water (D.M.W.) in a volume ratio 2 : 1 and the *p*H of the resultant gel was fixed ~ 1 by adding sodium hydroxide, with constant stirring. After keeping the gel for 24 hours at room temperature (~ 30°C), it was filtered, washed with DMW and dried in an air oven at 45°C. The product thus obtained was cracked in DMW to form the small granules and was treated with 1M HNO_3 for 24 hrs, with occasional shaking and replacing the acid, to convert it into the H^+ form. The excess acid was washed out and the material was finally dried at 45°C. Its Ba^{2+} and Sr^{2+} exchange capacities were found to be 1.61 and 1.59 meq/dry gram respectively as determined by the usual column process.

Equilibrium experiments

0.2 g fractions of the exchanger in H^+ form were shaken in various stoppered conical flasks at the desired temperatures (25° and 50°C), for one hour, with 20ml fractions of the metal solutions having a constant ionic strength (0.03M) adjusted by adding the appropriate amounts of HNO_3. The supernatant solution was analysed for the metal and hydrogen ions.

Results and Discussion

As it is clear from Fig. 1, the exchange equilibrium on antimony(V) silicate (SbSi) appears to have attained within an hour and hence all the equilibrium

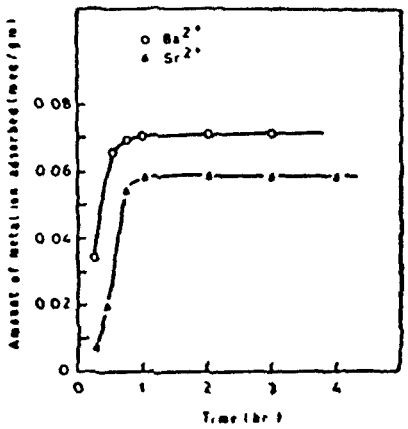


Fig. 1. A plot of the amount of Ba^{2+} and Sr^{2+} adsorbed on antimony(V) silicate vs time.

studies were performed after shaking for 1 hour. The interactions may be described as follows :

$$\bar{C}_H + C_M \rightleftharpoons \bar{C}_M + C_H, \qquad \ldots(1)$$

where the barred and unbarred quantities represent the equivalent concentrations in the exchanger and solution phases respectively. M stands for the metal ions (Ba^{2+} and Sr^{2+}). The equivalent ionic fractions of the counter ions in the SbSi and solution phases $\bar{X}_M$, $\bar{X}_H$, X_M and X_H were calculated by the expressions :

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}}, \; X_M = \frac{C_M}{C}, \; \bar{X}_H = \frac{\bar{C}_H}{\bar{C}}, \; X_H = \frac{C_H}{C},$$

where $\bar{C}$ and C are the total electrolyte concentrations in the solid and solution phases respectively.

To examine the affinity for the interacting ions, the separation factors and selectivity coefficients were calculated (Robinson & Stokes, 1959) by the following equations, assuming the ratio of the activity coefficients in solution to be unity (Singhal *et al.*, 1976). Under these conditions Kc ceases to express interactions in solution.

Now,
$$\alpha_H^M = \frac{\bar{X}_M}{\bar{X}_H} \cdot \frac{X_H}{X_M} \qquad \ldots(2)$$

and

$$Kc = \frac{\bar{X}_M}{(\bar{X}_H)^2} \cdot \frac{(X_H)^2}{X_M} \qquad \ldots(3)$$

The various values obtained at 25° and 50°C are summarized in Tables I and II and the exchange isotherms are shown in Fig. 2. For the Ba^{2+}-H^+ exchange at both the temperatures the isotherms are sigmoid indicating a selectivity reversal. Barium is preferred by the exchanger upto a certain value of the ionic fraction (0.60 at 25° and 0.64 at 50°C). Thereafter, it shows a preference for H^+ ions. However, in

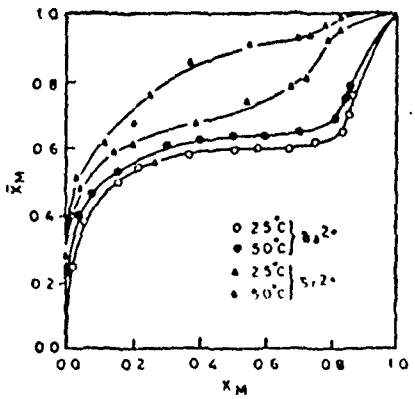


FIG. 2. Exchange isotherms of the $Ba^{2+}-H^+$ and $Sr^{2+}-H^+$ exchanges on antimony(V) silicate.

the Sr^{2+}-H^+ exchange Sr^{2+} ions are adsorbed preferably by the solid phase at all concentrations, the preference being higher at a higher temperature (Tables I and II).

TABLE I

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 25° and 50°C for the Ba^{2+}-H^+ exchange on antimony(V) silicate

Sl. No.	$\bar{X}_{Ba}$	X_{Ba}	$\bar{X}_{H}$	X_{H}	α_H^{Ba}	K_C	log K_C
				At 25°C			
1.	0.25	0.02	0.74	0.98	15.15	20.08	1.30
2.	0.38	0.05	0.63	0.94	10.72	15.96	1.20
3.	0.50	0.15	0.52	0.91	5.63	9.76	0.99
4.	0.54	0.23	0.48	0.82	4.13	7.10	0.85
5.	0.58	0.37	0.44	0.74	2.64	4.42	0.65
6.	0.60	0.51	0 42	0.66	1.84	2.90	0.46
7.	0.60	0.58	0.40	0.60	1.57	2.24	0.35
8.	0.60	0.67	0.38	0.55	1.31	1.90	0.28
9.	0.62	0.75	0.36	0.51	1.15	1.60	0.20
10.	0.65	0.83	0.33	0.15	0.35	0.15	−0.81
11.	0.70	0.85	0.30	0.13	0.35	0.15	−0.83
12.	0.76	0.86	0.24	0.13	0.46	0.24	−0.62
				At 50°C			
1.	0.24	0.01	0.75	0.99	31.52	41.51	1.62
2.	0.41	0.04	0.64	0.99	17.64	65.04	1.81
3.	0.46	0.07	0.54	0.93	1.12	19.25	1.28
4.	0.53	0.15	0.50	0.86	5.90	10.15	1.01
5.	0.61	0.30	0.47	0.77	3.27	5.33	0.73
6.	0.62	0.41	0.44	0.71	2.46	3.98	0.60
7.	0.64	0.50	0.42	0.64	1.91	2.89	0.46
8.	0.64	0.60	0.40	0.60	1.59	2.39	0.38
9.	0.65	0.70	0.37	0.57	1.44	2.22	0.35
10.	0.69	0.81	0.29	0.15	0.44	0.22	−0.65
11.	0.76	0.85	0.27	0.15	0.49	0.27	−0.57
12.	0.78	0.86	0 22	0.14	0.56	0.34	−0.47

The thermodynamic equilibrium constants were obtained (Gains & Thomas, 1953) from the relationship :

$$\ln K = (Z_A - Z_B) + \int_0^1 \ln K_C \, d\bar{X}_M, \qquad \ldots(4)$$

where Z_A and Z_B are the valencies of the competing ions. The integrals, evaluated from the areas under the curves (Fig. 3) using the trapezoidal rule (Singhal & Singh, 1977) are given in Table III. K values thus obtained are higher at higher temperature. Also, the values are higher for the Sr^{2+}-H^+ exchange as compared

TABLE II

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 25° and 50° C for the Sr^{2+}-H^+ exchange on antimony(V) silicate

Sl No.	$\bar{X}_{Sr}$	X_{Sr}	$\bar{X}_H$	X_H	α_H^{Sr}	K_C	log K_C
			At 25° C				
1.	0.27	0.01	0.73	0.99	36.62	49.65	1.69
2.	0.40	0.02	0.60	0.98	32.67	53.36	1.73
3.	0.48	0.04	0.52	0.96	22.15	40.90	1.61
4.	0.54	0.26	0.46	0.74	3.34	5.37	0.73
5.	0.59	0.14	0.41	0.86	8.84	18.54	1.27
6.	0.61	0.20	0.39	0.80	6.76	12.83	1.11
7.	0.67	0.39	0.33	0.61	3.18	5.87	0.77
8.	0.74	0.55	0.26	0.45	2.33	4.03	0.61
9.	0.78	0.68	0.22	0.32	1.67	2.42	0.39
10.	0.81	0.73	0.19	0.27	1.58	2.24	0.35
11.	0.92	0.79	0.08	0.20	2.91	7.28	0.86
12.	0.95	0.83	0.05	0.17	3.89	13.23	1.12
			At 50° C				
1.	0.28	0.01	0.72	1.00	38.89	54.01	1.73
2.	0.41	0.02	0.59	0.98	34.05	75.96	1.88
3.	0.51	0.03	0.49	0.97	33.65	66.62	1.82
4.	0.61	0.12	0.39	0.88	11.47	25.88	1.41
5.	0.68	0.20	0.32	0.80	8.50	21.25	1.33
6.	0.76	0.25	0.24	0.75	9.50	29.69	1.47
7.	0.86	0.37	0.14	0.63	10.46	47.07	1.67
8.	0.91	0.55	0.10	0.45	7.44	33.50	1.53
9.	0.92	0.70	0.08	0.30	4.93	18.48	1.27
10.	0.93	0.73	0.05	0.27	6.88	37.15	1.57
11.	0.97	0.78	0.03	0.20	8.29	55.27	1.74
12.	0.99	0.83	0.02	0.18	10.73	96.61	1.99

TABLE III

Thermodynamic values for the Ba^{2+}-H^+ and Sr^{2+}-H^+ exchanges on antimony(V) silicate at 25° and 50°C

Thermodynamic parameters	Values in Ba^{2+}-H^+ system		Values in Sr^{2+}-H^+ system	
	25°C	50°C	25°C	50°C
K	5.35	6.64	13.68	26.95
$\Delta G°$ (KJ mol^{-1})	−4.17	−5.09	−6.49	−8.89
$\Delta H°$ (KJ mol^{-1})	6.87		21.73	
$\Delta S°$ (KJ mol^{-1} degree^{-1})	0.04	0.04	0.09	0.09

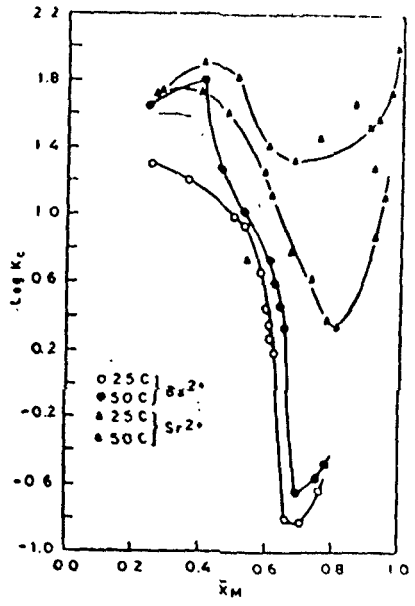


FIG. 3. A plot of log K_c *vs* $\bar{X}_M$ on antimony(V) silicate.

to the Ba^{2+}-H^+ exchange indicating a higher affinity of the exchanger for Sr^{2+} ions.

The standard free energies of exchange ($\Delta G°$) for the interaction (1) were calculated (Glasstone, 1960) using the relation :

$$\Delta G° = -RT \ln K, \qquad ...(5)$$

where R is the universal gas constant and T is the temperature in degrees Kelvin.

The standard enthalpy changes ($\Delta H°$) were then calculated from the Van't Hoff isochore :

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad ...(6)$$

and standard entropy changes ($\Delta S°$), by the equation :

$$\Delta G° = \Delta H° - T\Delta S° \qquad ...(7)$$

A negative free energy change (Table III) for both the interactions means that these ions are adsorbed preferably as compared to the H^+-ions on SbSi. Also, the adsorption increases with temperature. A positive enthalpy change in both the interactions confirms this view.

The activity coefficients of the metal and H^+ ions were calculated (El-Sayed *et al.*, 1970; and Howery & Thomas, 1965) from the following expressions :

$$\ln f_M = (\bar{X}_M - 1) \ln Kc - \int_0^{\bar{X}_M} \ln Kc \, d\bar{X}_M \qquad ...(8)$$

$$\ln f_H = \bar{X}_M \ln Kc - \int_0^{\bar{X}_M} \ln Kc \, d\bar{X}_M \qquad \ldots(9)$$

and the values are tabulated in Table IV.

TABLE IV

Values of the activity coefficients for the different Ba^{2+}-H^+ and Sr^{2+}-H^+ exchanges on antimony(V) silicate at 25° and 50°C

Sl. No.	Values at 25°C			Values at 50°C		
	$\bar{X}_{Ba}$	f_{Ba}	f_H	$\bar{X}_{Ba}$	f_{Ba}	f_H
			Ba^{2+}-H^+			
1.	0.25	0.10	2.10	0.24	0.06	2.44
2.	0.38	0.12	1.99	0.41	0.05	3.22
3.	0.50	0.16	1.59	0.46	0.10	1.99
4.	0.54	0.19	1.34	0.53	0.14	1.39
5.	0.58	0.23	1.02	0 61	0.19	1.03
6.	0.60	0.27	0.80	0.62	0.24	0.87
7.	0.60	0.29	0.61	0.64	0.24	0.70
8.	0.60	0.31	0.63	0.64	0.24	0.70
9.	0.62	0.35	0.55	0.65	0.27	0.59
10.	0.65	0.80	0.12	0.69	0.57	0.13
11.	0.70	0.82	0.12	0.76	2.54	0.15
12.	0.76	0.71	0.35	0.78	0.52	0.18

Sl. No.	Values at 25°C			Values at 50°C		
	$\bar{X}_{Sr}$	f_{Sr}	f_H	$\bar{X}_{Sr}$	f_{Sr}	f_H
			Sr^{2+}-H^+			
1.	0.27	0.06	2.81	0.28	0.06	2.99
2.	0.40	0.07	3.72	0.41	0.05	3.88
3.	0.48	0.08	3.31	0.51	0.06	4.11
4.	0.54	0.22	1.17	0.61	0.08	2.09
5.	0.59	0.12	2.26	0.68	0.08	2.99
6.	0.61	0.14	1.76	0.76	0.08	3.61
7.	0.67	0.16	0.94	0.86	0.07	2.08
8.	0.74	0.19	0.77	0.91	0.10	3.49
9.	0.78	0.20	0.49	0.92	0.11	2.03
10.	0.81	0.22	0.48	0.93	0.10	3.84
11.	0.92	0.18	1.35	0.97	0.10	4.59
12.	0.95	0.17	2.13	0.99	0.10	5.90

At both the temperatures, the f_M values are less than unity Further, a variation in f_H values is observed in both the cases indicating a heterogeneity in the distribution of ions on SbSi surface during the ion-exchange process similar to the soils reported by Diest and Talibudden (1967)

To further examine the deviation of these heterogeneous systems from ideality, the excess thermodynamic functions (Tables V and VI) were calculated (Gast & Klobe, 1971; and Vanselow, 1932) from the expressions :

TABLE V

Values of the excess free energies, enthalpies and entropies of mixing for the Ba^{++}-H^+ exchange on antimony(V) silicate at 25° and 50°C

Sl No	$\bar{X}_{B_a}$	ΔG^{ex}_m (KJ mol^{-1})	ΔH^{ex}_m (KJ mol^{-1})	ΔS^{ex}_m (KJ mol^{-1} degree^{-1})
		At 25°C		
1.	0 25	−0 05	1 07	0 00
2	0 38	−0 86	1 33	0 01
3	0 50	−1 66	3 32	0 02
4.	0 54	−1 88	4 74	0 02
5.	0 58	−2 07	3 17	0 02
6	0 60	−2.16	1 01	0 01
7.	0 60	−2 46	1 69	0 01
8.	0 60	−2 17	3 52	0 02
9.	0 62	−2 17	4 05	0 02
10	0 65	−2 07	6 26	0 03
11.	0 70	−1 95	6 61	0 03
12.	0.76	−1.27	12 24	0 05
		At 50°C		
1.	0 24	−0 04	1 02	0 00
2.	0 41	−1 25	2 30	0 01
3.	0 46	−1 81	6 87	0 03
4.	0 53	−3 25	5 38	0 03
5	0.61	−2 67	3 96	0 02
6.	0 62	−2 53	1 21	0 01
7.	0 64	−2 84	2 08	0 02
8.	0 64	−2 81	4 37	0 02
9.	0 65	−2 83	5 02	0 02
10.	0 69	−2 66	7 91	0 03
11	0 76	−2 61	8 81	0 04
12.	0 78	−2 43	14 12	0 05

$$\Delta G^{ex}_m = RT(\bar{X}_M \ln f_M + \bar{X}_H \ln f_H) \quad . \quad (10)$$

$$\Delta H^{ex}_m = -RT^2\left[\bar{X}_M\left(\frac{\delta \ln f_M}{\delta T}\right) + \bar{X}_H\left(\frac{\delta \ln f_H}{\delta T}\right)\right] \quad .. \quad (11)$$

TABLE VI

Values of the excess free energies, enthalpies and entropies of mixing for the Sr^{2+}-H^+ exchange on antimony(V) silicate at 25° and 50°C

Sl. No.	X_{Sr}	ΔG_m^E (KJ mol^{-1})	ΔH_m^E (KJ mol^{-1})	ΔS_m^E (KJ mol^{-1} degree^{-1})
		At 25°C		
1.	0.27	−0.05	−0.12	−0.00
2.	0.40	−0.69	−2.89	−0.01
3.	0.48	−1.45	0.42	0.01
4.	0.54	−1.87	56.68	0.20
5.	0.59	−2.25	4.11	0.02
6.	0.61	−2.46	0.86	0.01
7.	0.67	−3.10	9.14	0.04
8.	0.74	−3.22	1.54	0.02
9.	0.78	−3.47	5.03	0.03
10.	0.81	−3.43	5.88	0.03
11.	0.92	−3.78	13.56	0.06
12.	0.95	−4.02	11.20	0.06
		At 50°C		
1.	0.28	−0.05	−1.37	−0.00
2.	0.41	−1.13	3.52	0.01
3.	0.51	−1.94	0.99	0.01
4.	0.61	−3.35	77.84	0.25
5.	0.68	−3.69	7.05	0.03
6.	6.76	−4.26	7.38	0.04
7.	0.86	−5.93	21.60	0.09
8.	0.91	−5.20	13.78	0.06
9.	0.92	−5.32	15.79	0.07
10.	0.93	−5.49	20.11	0.08
11.	0.97	−5.85	19.11	0.08
12.	0.99	−6.14	19.62	0.08

and

$$\Delta G_m^E = \Delta H_m^E - T\Delta S_m^E, \qquad \ldots(12)$$

where ΔG_m^E, ΔH_m^E and ΔS_m^E are the excess free energies, enthalpies and entropies of mixing. As it is clear from Tables V and VI the ΔG_m^E values are negative at both the temperatures studied for the Ba^{2+}-H^+ and Sr^{2+}-H^+ exchanges. It indicates that the heterogeneous mixture of ions during the exchange is more stable as compared to the pure forms. Further, the stability increases with a rise in the concentration of $\bar{X}_M$ in case of the Sr^{2+}-H^+ exchange. It also appears to be true for the Ba^{2+}-H^+ exchange but to a limited extent (upto $\bar{X}_{Ba} = 0.60$). The values of enthalpies and entropies of mixing suggest that the Sr^{2+}-H^+ ions are more strongly bound

on the SbSi surface than the Ba^{2+}-H^+ ions. The observations are in agreement with those of Howery and Thomas (1965) on clays.

ACKNOWLEDGEMENT

The authors are grateful to Professor M. Qureshi for providing research facilities and to the C. S. I. R. (India) for the financial assistance to one of us (S.R.).

REFERENCES

Alberti, G., and Costantino, U. (1974) Forward and reverse lithium-potassium ion-exchange isotherms of crystalline zirconium phosphate. *J. inorg. nucl. Chem.*, **36**, 653–659.

Baetstle, L. (1963) Ion-exchange properties of zirconyl phosphates-III. Influence of temperature on tracer ion-equilibria. *J. inorg. nucl. Chem.*, **25**, 271–282.

Diest, J., and Talibuddeen, O. (1967) Ion-exchange in soils for the ion-pairs K-Ca, C-Rb and K-Na. *J. Soil Sci.*, **18**, 125–137.

El-Sayed, M. H., Burau, R. G., and Babcock, K. L. (1970) Thermodynamics of copper (II)-calcium exchange on bentonite clay. *Soil Sci. Soc. Amer. Proc.*, **34**, 397–400.

Gains, G. L., and Thomas, H. C. (1953) Adsorption studies on clay minerals II. A formation of the thermodynamics of exchange adsorption. *J. chem. Phys.*, **21**, 714–718.

Gast, R. G., and Klobe, W. D. (1971) Sodium-lithium exchange equilibria on vermiculite at 25 and 50°C. *Clays and Clay Min.*, **19**, 311–319.

Glasstone, S. (1960) *Text Book of Physical Chemistry*, p. 827. Macmillan and Co. Ltd, London.

Howery, D. G., and Thomas, H. C. (1965) Ion-exchange on mineral clinoptilolite. *J. phys. Chem.* **69**, 531–537.

Larsen, E. M., and Vissers, D. R. (1960) The exchange of Li^+, Na^+, and K^+ with H^+ on zirconium phosphate. *J. phys. Chem.*, **64**, 1732–1736.

Nancollas, G. H., and Tilak, B. V. K. S. R. A. (1969) Thermodynamics of cation exchange on semi-crystalline zirconium phosphate. *J. inorg. nucl. Chem.*, **31**, 3643–3653.

Rawat, J. P., and Thind, P. S. (1980) Thermodynamics of cation exchange. *J. Indian chem. Soc.*, **57**, 819–822.

Rawat, J. P., and Muktawat, K. P. S. (1981) Thermodynamics of ion-exchange on ferric antimonate. *J. inorg. nucl. Chem.*, **43**, 2121–2128.

Robinson, R. A., and Stokes, R. H. (1959) *Electrolyte Solutions*. p. 481, Butterworths, London.

Singhal, J. P., Singh, R. P., Singh, C. P., and Gupta, G. K. (1976) Thermodynamics of the exchange of nicotine on aluminium montmorillonite. *J. Soil Sci.*, **27**, 42–47.

Singhal, J. P., and Singh, R. P. (1977) Aluminium-nicotine exchange equilibria: Part III – on kaolinite. *Acta. Chim. Acad.*, **93**, 307–314.

Vanselow, A. P. (1932) Equilibrium of the base-exchange reactions of bentonites, permutites, soil colloids and zeolites. *Soil. Sci.*, **33**, 95–113.

Varshney, K. G., Sharma, U., Rani, S., and Premadas, A. (1982–83) Cation-exchange study on a crystalline and thermally stable phase of antimony silicate. *Sepn. Sci. & Tech.*, **17**, 1527–1543.

Walton, H. F. (1980) Ion exchange and liquid column chromatography. *Anal. Chem.*, **52**, 15R–27R.

4·3 Adsorption Thermodynamics of Carbofuran on Antimony (V) Silicate Cation Exchanger

K. G. VARSHNEY, SIMA RANI, AND R. P. SINGH*

*Analytical Laboratories, Chemistry Section, Faculty of Engineering & Technology, and *Section of Plant Pathology and Nematology, Botany Department, Aligarh Muslim University, Aligarh 202001, India*

Received July 29, 1985

The adsorption thermodynamics of carbofuran has been studied on antimony (V) silicate cation exchanger at 30 and 50°C. The adsorption isotherms of carbofuran have been found to follow the Freundlich adsorption model and yield "S" class isotherms. The order of adsorption of carbofuran is in accordance with the partial molal free-energy changes in the exchanger. The thermodynamic equilibrium constant (K_0), standard free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes have also been calculated for predicting the nature of adsorption.

INTRODUCTION

The adsorption of pesticides on soils has been a significant feature (Bailey and White, 1970; Biggar and Cheung, 1973; Nearpass, 1965; Van Bladal and Moreale, 1974) which is affected by the presence of metal ions in soils as they have an important role in modifying its nutritional status. Inorganic materials possessing ion exchange properties are known to be selective for various metal ions (Walton, 1980) and hence their presence in soil may have some far reaching consequences for its more judicious use in field crops. Adsorption behavior of inorganic ion exchangers for pesticides is, therefore, an important aspect of study which has so far been lacking. The present paper summarizes our effort in selecting antimony (V) silicate as an adsorbent and carbofuran as an adsorbing species. Antimony (V) silicate possesses a high selectivity for alkaline earths (Varshney *et al.*, 1982) and a promising chemical stability, while carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuramyl methyl carbamate) has been the least studied pesticide for its adsorption behavior (Felsot and Wilson, 1980; Jamet and Piedallu, 1975; Singh *et al.*, 1985).

EXPERIMENTAL

Reagents and chemicals. Antimony (V) chloride and sodium silicate were the products of Koch Light Laboratories Ltd. (Colonbrook Bucks, England) and Riedal (Dehaenag, Seelze Hannover), respectively. Carbofuran/Furadon-3G was obtained from Rallis India Ltd., Bombay. All other reagents and chemicals were of BDH (A.R.) grade.

Apparatus. A shaking water bath incubator having a temperature variation of ± 0.1°C was used for all the equilibrium studies, and the Bausch and Lomb Spectronic-20 spectrophotometer for the spectrophotometric studies.

Synthesis of antimony (V) silicate (SbSi). A 0.1 *M* solution of antimony (V) chloride in 4 *M* HCl was mixed with a 0.1 *M* solution of sodium silicate in demineralized

0147-6513/86 $3.00

water (DMW) in a volume ratio 2:1, and the pH (~1) of the resulting gel was adjusted by adding sodium hydroxide with constant stirring. After 24 hr the gel was filtered, washed, and dried in an air oven at 45°C. It was then cracked into small granules by addition of DMW, and converted into the H^+ form by treating with 1 *M* HNO_3 for 24 hr with occasional shaking and intermittently replacing the acid. The material thus obtained was finally washed to remove the excess acid and then dried at 45°C as above. Its Na^+ ion exchange capacity, determined by the usual column process, was found to be 1.6 meq/g.

Adsorption studies. Fractions (0.2 g) of the SbSi (H^+ form) were taken in various stoppered conical flasks at the desired temperature (30 or 50°C) followed by the carbofuran solution (2500 μg/ml in CH_3OH) in varying amounts (0 to 10 ml). The total volume was brought to 20 ml by adding DMW and the contents were shaken for 2 hr. The supernatant liquid was then analyzed spectrophotometrically (Mithyantha and Perur, 1974) for the presence of carbofuran.

RESULTS

Adsorption of carbofuran on antimony (V) silicate at 30 and 50°C is represented by the adsorption isotherms (Fig. 1) which are concave to the *Y* axis up to an equilibrium concentration ~1.12×10^{-3} mmol/ml. Above this concentration a reversal is obtained. The adsorption decreases with a rise in temperature. The average partial molal free energy changes, obtained from the thermodynamic relationship

$$-F = RT \ln \frac{C_e}{C_0} \tag{1}$$

where C_e and C_0 are the equilibrium and initial concentrations of the carbofuran in the suspension (1603.96 and 1641.89 at 30 and 50°C, respectively).

The adsorption behavior of carbofuran is in close agreement with the Freundlich equation

$$x/m = KC^{1/n} \tag{2}$$

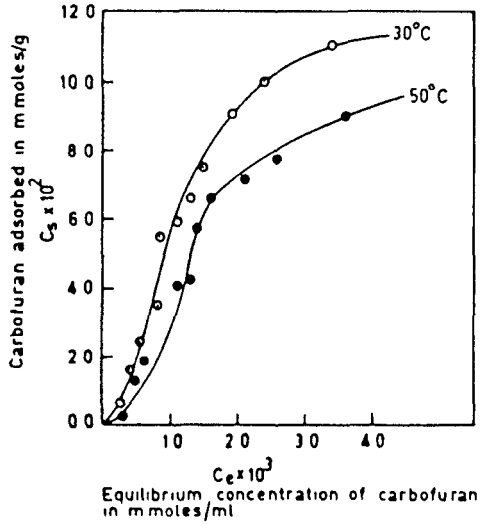


FIG. 1. Adsorption isotherms of carbofuran on antimony (V) silicate cation exchanger at 30 and 50°C

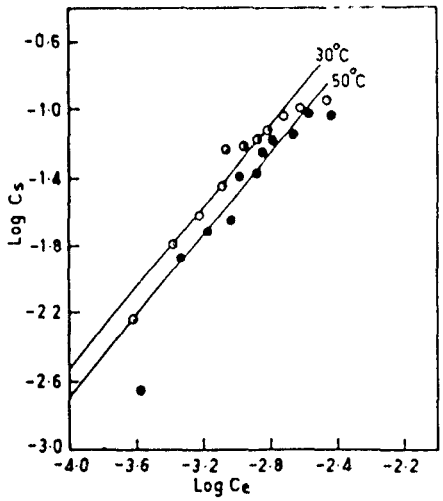


FIG. 2. Freundlich isotherms of carbofuran adsorption on antimony (V) silicate cation exchanger at 30 and 50°C.

where x/m = millimoles of carbofuran adsorbed per gram of SbSi, C is the concentration of carbofuran in equilibrium suspension per ml, K and $1/n$ are the constants evaluated from the intercept and slope of the curves (Fig. 2), respectively. The values are summarized in Table 1.

The thermodynamic equilibrium constant (K_0) for the adsorption reaction was obtained by plotting ln (C_s/C_e) versus C_s and extrapolating C_s to zero (Biggar and Cheung, 1973), where C_s = millimoles of carbofuran adsorbed per gram, and C_e = millimoles of carbofuran per milliliter in equilibrium suspension.

The standard free energy changes ($\Delta G°$) for the interaction were calculated (Glasstone, 1960) from the relationship

$$\Delta G° = -RT \ln K_0 \tag{3}$$

where R is the universal gas constant and T is the temperature in degrees Kelvin. The standard enthalpy changes ($\Delta H°$) were then calculated from the Van't Hoff isochore

$$\ln \left[\frac{K_0 T_2}{K_0 T_1}\right] = -\frac{\Delta H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{4}$$

TABLE 1

FREUNDLICH ISOTHERM CONSTANTS K AND $1/n$ FOR THE ADSORPTION OF CARBOFURAN ON ANTIMONY (V) SILICATE CATION EXCHANGER AT 30 AND 50°C

	Temperature	
Freundlich isotherm constants	30°C	50°C
K	3.02×10^{-3}	1.995×10^{-3}
$1/n$	1.1881	1.2000

TABLE 2

VALUES OF THE VARIOUS THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF CARBOFURAN ON ANTIMONY (V) SILICATE CATION EXCHANGER AT 30 AND 50°C

Thermodynamic equilibrium constants	Temperature	
	30°C	50°C
K_0	1 5300	1 3648
$\Delta G°$ (Cal/mol)	−256 3828	−199 9272
$\Delta H°$ (Cal/mol)	−1111 6861	
$\Delta S°$ (Cal/mol/deg)	−2.8228	

and standard entropy changes ($\Delta S°$) by the equation

$$\Delta G° = \Delta H° - T\Delta S°. \quad (5)$$

Table 2 summarizes the values of the various parameters obtained as above

DISCUSSION

It is clear from Fig. 1 that the adsorption of carbofuran is higher at a lower temperature. Also, it is easier at a higher equilibrium concentration range of carbofuran. Thus, the adsorption behavior of SbSi is essentially similar to that of the sandy clay loam and silt loam soils (Singh *et al*, 1985). However, the extent of adsorption is much higher on SbSi. It is, perhaps, due to a high adsorption capacity (approx. 10 times) of the exchanger as compared to the soils.

CONCLUSION

Therefore, the study indicates that the presence of an inorganic material possessing a good ion exchange capacity enhances the adsorption characteristic of the soil, thus retarding effectively the movement of a pesticide which may, otherwise, have a harmful effect on crops.

ACKNOWLEDGMENTS

The authors thank Dr K. T Nasim and Professor S K. Saxena for providing research facilities, and the CSIR (India) for financial assistance.

REFERENCES

BAILEY, G. W., AND WHITE, J. L. (1970) Factors influencing the adsorption, desorption and movement of pesticides in soil. *Residue Rev* 32, 29–92

BIGGAR, J. W., AND CHEUNG, M. W (1973) Adsorption of picloram (4-amino-3,5,6-trichloropicolinic acid) on panoche, ephrata and palous soils A thermodynamic approach to the adsorption mechanism *Soil Sci Soc Amer Proc* 37, 863–868

FELSOT, A., AND WILSON, J. (1980) Adsorption of carbofuran and movement on soil thin layers *Bull Environ Contam Toxicol* 24, 778–782.

GLASSTONE, S (1960). *Text book of Physical Chemistry*. 2nd Ed., pp 815–883 Van Nostrand, New York

HELLING, C. S., AND TURNER, B C (1968) Pesticide mobility: Determination by soil thin-layer chromatography. *Science (Washington D C)* 162, 562–563

A8004 T-38,39,40T EES 615 4

JAS

JAMET, P, AND PIEDALLU, M A (1975) Movement of carbofuran in different types of soil Study of adsorption and desorption of carbofuran *Phytiatr Phytopharm* **24**, 279–295

MITHYANTHA, M S, AND PERUR, N S (1974) A new colorimetric method for the estimation of carbofuran in pesticide formations *Curr Sci* **43**, 578

NEARPASS, D C (1965) Effect of soil activity on the adsorption penetration and persistance of simazine *Weeds* **13**, 341–346

SINGH, R P, KHAN, A M, AND SAXENA S K (1977) Effect of different factors on the movement of nematicides in Aligarh soil using thin-layer chromatography *Indian J Nematol* **7**, 140–144

SINGH, R P, VARSHNEY, K G, AND RANI, S (1985) Adsorption thermodynamics of carbofuran on sandy clay loam and silt loam soils *Ecotoxicol Environ Saf* **10**, 309–313

VAN BLADEL, R, AND MOREALE, A (1974) Adsorption of Fenuron and Monuron (substituted ureas) by two montmorillonite clays *Soil Sci Soc Amer Proc* **38**, 244–249

VARSHNEY, K G, SHARMA, U, RANI, S, AND PREMADAS, A (1982) Cation-exchange study on a crystalline and thermally stable phase of antimony silicate Effect of irradiation on ion-exchange behaviour and separation of Cd(II) from Zn(II) and Mn(II) and of Mg(II) from Ba(II) Ca(II) and Sr(II) *Sep Sci Technol* **17**, 1527–1543

WALTON, H F (1980) Ion exchange and liquid column chromatography *Anal Chem* **52**, 15R–27R

© *Proc. Indian natn. Sci. Acad.*, **51**, A, No. 4, 1985, pp 726-734.
Printed in India.

4·4

THERMODYNAMICS OF THE Ba^{2+}-H^+ AND Sr^{2+}-H^+ EXCHANGES ON ZIRCONIUM(IV) PHOSPHOSILICATE CATION EXCHANGER

K G VARSHNEY,* R P SINGH** *and* UMA SHARMA

Analytical Laboratories, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001, INDIA

(Received 5 July 1984)

A thermodynamic study has been made on the exchange of Ba^{2+} and Sr^{2+} ions with the zirconium(IV) phosphosilicate in H^+-form at 30 and 50 °C which gives various thermodynamic parameters for the processes taking place in the material. The excess free energies (ΔG_m^x), enthalpies (ΔH_m^x) and entropies (ΔS_m^x) of mixing have also been evaluated.

Key Words : Thermodynamics; Cation Exchange; Zirconium(IV) Phosphosilicate

INTRODUCTION

INORGANIC ion exchangers are generally used for the metal ion separations. Although a large number of such materials have been synthesized,[1] only few of them have been studied thermodynamically.[2–7] Zirconium (IV) phosphosilicate (ZPS) has shown a semi-crystalline nature, promising ion exchange behaviour and reproducibility.[8] A thermodynamic study on this material should, therefore, be helpful to understand the ion-exchange mechanism underlying in this material.

EXPERIMENTAL

Reagents

Zirconyl chloride and sodium silicate were the B.D.H.(England) and Reidel (DEHAENAG, Seelze, Hannover) products respectively. All other reagents and chemicals were of Analar grade.

Apparatus

A water bath incubator shaker having a temperature variation of ± 0.5 °C was used for the equilibrium studies.

*Author for all correspondence.
**Section of Plant Pathology and Nematology, Department of Botany, Aligarh Muslim University, Aligarh.

Synthesis of Zirconium(IV) Phosphosilicate (ZPS)

It was synthesized by the method described earlier.[7]

Equilibrium Experiments

0.2 g samples of the exchanger in H^+ form were shaken in several stoppered conical flasks at the desired temperatures (30°C and 50°C) for 12hr with the 20ml fractions of metal ion solution having a constant ionic strength (0.03M) by adding appropriate amount of HNO_3 and the supernatant liquids were analysed for the metal and hydrogen ions volumetrically.

Evaluation of Thermodynamic Quantities

The ion-exchange process occurring on ZPS can be represented by the equation

$$2H^+ZPS + M^{2+} \rightleftharpoons M^+ - (ZPS)_2 + 2H^+, \qquad \ldots(1)$$

where M^{2+} represents the Ba^{2+} and Sr^{2+} ions. The equilibrium between the ionic concentrations in the exchanger and solution phases can be represented as :

$$\bar{C}_H + C_M \rightleftharpoons \bar{C}_M + C_H \qquad \ldots(2)$$

and the equivalent ionic fractions of metal ions in the two phases can be calculated from the expressions :

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}}, \; X_M = \frac{C_M}{C}, \; \bar{X}_H = \frac{\bar{C}_H}{\bar{C}_H}, X_H = \frac{C_H}{C}. \qquad \ldots(3)$$

Then, the separation factors can be calculated using the relation

$$\alpha_H^M = \frac{\bar{X}_M}{\bar{X}_H} \cdot \frac{X_H}{X_M}. \qquad \ldots(4)$$

Since the solutions were taken in the dilute range of concentrations, the selectivity coefficients can be calculated from the expression

$$Kc = \frac{\bar{X}_M}{\bar{X}_H^2} \cdot \frac{X_H^2}{X_M} \qquad \ldots(5)$$

taking the ratio of activity coefficients as unity.[9] The thermodynamic equilibrium constant K can be obtained[10] from the equation :

$$\ln K = (Z_A - Z_B) + \int_0^1 \ln Kc d\bar{X}_M \qquad \ldots(6)$$

The thermodynamic functions ($\Delta G°$, $\Delta H°$ and $\Delta S°$) can be calculated by utilizing the Van't Hoff reaction isotherm for $\Delta G°$, the Van't Hoff isochore for $\Delta H°$ and the Gibbs-Helmholtz equation for $\Delta S°$.[11]

The activity coefficients of metal and hydrogen ions can be calculated from the expression[12]

$$\ln f_M = (\bar{X}_M - 1) \ln K_C - \int_0^{\bar{X}_M} \ln K_C \, d\bar{X}_M \qquad ...(7)$$

and $$\ln f_H = \bar{X}_M \ln K_C - \int_0^{\bar{X}_M} \ln K_C \, d\bar{X}_M \qquad ...(8)$$

and the excess thermodynamic functions from the relations.[13,14]

$$\Delta G_m^E = RT\left[\bar{X}_M \ln f_M + \bar{X}_H \ln f_H\right], \qquad ...(9)$$

$$\Delta H_m^E = -RT^2\left[\bar{X}_M\left(\frac{\ln f_M}{T}\right) + \bar{X}_H\left(\frac{\ln f_H}{T}\right)\right] \qquad ...(10)$$

and $$\Delta G_m^E = \Delta H_m^E - T\Delta S_m^E . \qquad ...(11)$$

Results and Discussion

The values of equivalent ionic fractions at 30 and 50 °C calculated for Ba^{2+} and Sr^{2+} exchanges in H^+-ZPS applying equation (3) are summarized in Tables I and II and the exchange isotherms are shown in Figs. 1 and 2. As Fig. 1 illustrates the Ba^{2+}-H^+ exchange isotherms are sigmoid and show a selectivity reversal at both the temperatures. It suggests that hydrogen ions are strongly preferred by ZPS upto an equivalent ionic fraction of 0.60 at 30 °C and upto 0.49 at 50 °C. Thereafter, an upward trend is observed for the Ba^{2+} ions. In case of the Sr^{2+}-H^+ exchange (Fig. 2) the isotherms are of Langmuir type. They show a stronger preference for H^+ as compared to Sr^{2+} throughout the range of concentration studied and the affinity is affected by temperature, being higher at 30 °C. It is supported by the separation factors (Table II) also. For the Ba^{2+}-H^+ exchange (Table I), however, some values of separation factor are greater than unity, indicating a selectivity reversal (Fig. 1).

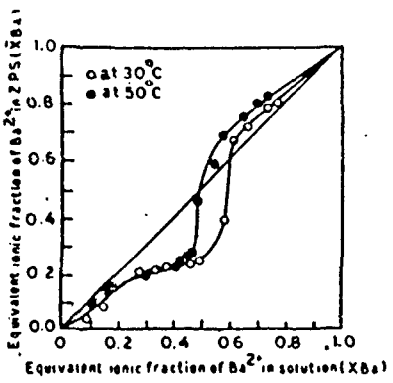


Fig 1 Exchange isotherms of Ba^{2+}-H^+ on *ZPS* at 30 and 50 °C

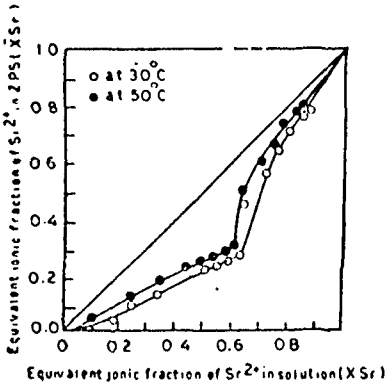


Fig 2 Exchange isotherms of Sr^{2+}-H^+ on *ZPS* at 30 and 50 °C

TABLE I

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 30° and 50 °C for the Ba^{2+}-H^+ exchange on zirconium(IV) phosphosilicate

Sl. No.	$\bar{X}_{Ba}$	X_{Ba}	$\bar{X}_H$	X_H	α_H^{Ba}	K_c	log K_c
				At 30 °C			
1.	0.04	0.08	0.96	0.92	0.50	0.45	−0.35
2.	0.09	0.14	0.91	0.86	0.60	0.54	−0.27
3.	0.16	0.16	0.84	0.84	0.99	0.96	−0.19
4.	0.16	0.25	0.84	0.75	0.55	0.47	−0.33
5.	0.21	0.27	0.79	0.73	0.52	0.65	−0.19
6.	0.22	0.33	0.79	0.97	0.55	0.45	−0.35
7.	0.23	0.37	0.77	0.63	3.52	0.42	−0.37
8.	0.24	0.43	0.76	0.57	0.42	0.32	−0.50
9.	0.24	0.46	0.76	0.55	0.36	0.28	−0.55
10.	0.25	0.49	0.75	0.51	0.35	0.24	−0.62
11.	0.39	0.53	0.61	0.47	0.58	0.45	−0.35
12.	0.40	0.58	0.30	0.42	0.87	1.31	+0.12
13.	0.67	0.61	0.33	0.39	1.40	1.55	+0.19
14.	0.72	0.63	0.28	0.34	1.34	1.65	+0.22
15.	0.79	0.73	0.21	0.27	1.46	1.96	+0.29
16.	0.80	0.77	0.20	0.23	0.98	1.45	+0.16
				At 50 °C			
1.	0.07	0.02	0.93	0.98	3.38	3.37	+0.53
2.	0.12	0.10	0.88	0.90	1.24	1.21	+0.08
3.	0.15	0.16	0.85	0.84	0.92	0.83	−0.08
4.	0.15	0.28	0.85	0.72	0.47	0.37	−0.43
5.	0.20	0.30	0.80	0.70	0.57	0.48	−0.32
6.	0.22	0.34	0.78	0.66	0.57	0.48	−0.32
7.	0.23	0.41	0.77	0.60	0.43	0.32	−0.49
8.	0.26	0.42	0.74	0.59	0.51	0.39	−0.41
9.	0.26	0.45	0.74	0.55	0.44	0.33	−0.48
10.	0.27	0.46	0.73	0.52	0.21	0.29	−0.54
11.	0.47	0.48	0.53	0.52	0.96	0.94	−0.03
12.	0.59	0.55	0.41	0.45	1.17	0.29	+0.11
13.	0.68	0.57	0.32	0.43	1.58	2.11	+0.32
14.	0.74	0.64	0.26	0.36	1.60	2.22	+0.35
15.	0.80	0.71	0.20	0.29	1.63	2.36	+0.37
16.	0.82	0.74	0.18	0.26	1.56	2.24	+0.35

Values of selectivity coefficients (K_C) obtained with the help of equation (5) are summarized in Tables I and II while the plots of log K_C versus X_M are shown in Figs. 3 and 4. The thermodynamic equilibrium constants were then obtained from the equations 6. The integrals were evaluated from the areas under the curves of Figs. 3 and 4 using the trapezoidal rule,[15] the values being summarized in Table III. In both the systems the K values were higher at 50 °C than at 30 °C indicating a higher affinity of the exchanger for the Ba^{2+} and Sr^{2+} ions at a higher

TABLE II

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 30° and 50 °C for the Sr^{2+}-H^+ exchange on Zirconium(IV) phosphosilicate

Sl. No.	$\bar{X}_{Sr}$	X_{Sr}	$\bar{X}_{H}$	X_{H}	α_H^{Sr}	K_e	log K_e
			At 30 °C				
1.	0.04	0.17	0.96	0.86	0.21	0.17	- 0.77
2.	0.11	0.24	0.79	0.43	0.42	0.37	0.43
3.	0.15	0.33	0.85	0.76	0.41	0.35	- 0.46
4.	0.24	0.33	0.77	0.67	0.62	0.51	−0.29
5.	0.24	0.43	0.76	0.57	0.41	0.29	- 0.74
6.	0.24	0.51	0.76	0.49	0.31	0.20	−0.71
7.	0.25	0.54	0.76	0.46	0.80	0.17	−0.78
8.	0.26	0.58	0.74	0.42	0.26	0.15	−0.83
9.	0.27	0.62	0.73	0.38	0.23	0.12	0.53
10.	0.27	0.63	0.73	0.37	0.22	0.12	−0.96
11.	0.47	0.64	0.73	0.35	0.27	0.30	0.53
12.	0.57	0.72	0.44	0.28	0.51	0.32	−0.50
13.	0.65	0.76	0.35	0.24	0.57	0.38	-0.43
14.	0.72	0.79	0.28	0.21	0.67	0.48	0.32
15.	0.77	0.85	0.23	0.15	0.60	0.40	−0.40
16.	0.78	0.87	0.22	0.13	0.53	0.31	- 0.50
			At 50 °C				
1.	0.05	0.10	0.91	0.91	0.56	0.55	0.26
2.	0.12	0.24	0.88	0.76	0.45	0.37	- 0.43
3.	0.13	0.25	0.79	0.75	0.51	0.46	−0.34
4.	0.19	0.34	0.46	0.66	0.47	0.39	−0.41
5.	0.24	0.44	0.76	0.56	0.41	0.29	−0.55
6.	0.26	0.49	0.74	0.51	0.38	0.25	−0.50
7.	0.28	0.53	0.72	0.47	0 35	0.22	0.66
8.	0.29	0.57	0.71	0.43	0.30	1.18	0.76
9.	0.30	0.59	0.70	0.41	0.29	0.17	0.78
10.	0.33	0.60	0.67	0.40	0.32	0.18	−0.74
11.	0.51	0.63	0.49	0.37	0.61	0.45	0.35
12.	0.60	0.70	0.40	0.30	0.64	0.47	0.33
13.	0.67	0.75	0.33	0.25	0.68	0.50	- 0.31
14.	0.74	0.78	0.26	0.23	0.82	0.78	0.17
15.	0.78	0.84	0.22	0.16	0.68	0.19	0.31
16.	0.81	0.85	0.20	0.14	0 66	0.46	0.34

TABLE III

Thermodynamic values for the Ba^{2+}-H^+ and Sr^{2+}-H^+ exchanges on zirconium(IV) phosphosilicate at 30 °C and 50 °C

Thermodynamic parameters	Values in Ba^{2+}-H^+ system		Values in Sr^{2+}-H^+ system	
	30 °C	50 °C	30 °C	50 °C
K	2.12	2.54	1.08	1.41
ΔG° (KJ mol^{-1})	−1.89	2.51	−0.19	- 0.92
ΔH° (KJ mol^{-1})	7.40		10.83	
ΔS° (KJ mol^{-1} $degree^{-1}$)	0.03	0.03	0.04	0.04

TABLE IV

Values of the activity coefficients for the different Ba^{2+}-H^+ *and* Sr^{2+}-H^+ *exchanges on zirconium(IV) phosphosilicate at* 30 °C *and* 50 °C

Sl. No.	Values at 30 °C			Values at 50 °C		
	$\bar{X}_{Ba}$	f_{Ba}	f_H	$\bar{X}_{Ba}$	f_{Ba}	f_H
			Ba^{2+}-H^+			
1.	0.04	1.27	1.01	0.07	2.36	0.94
2.	0.09	1.12	1.02	0.12	1.35	1.00
3.	0.16	1.10	1.05	0.14	1.78	1.03
4.	0.16	1.10	1.05	0.14	1.78	1.03
5.	0.21	0.60	0.96	0.20	0.94	0.53
6.	0.22	1.93	0.92	0.22	2.03	0.91
7.	0.23	0.13	0.91	0.23	2.07	0.90
8.	0.24	2.92	0.82	0.26	2.55	0.84
9.	0.24	2.92	0.82	0.26	2.55	0.84
10.	0.25	2.25	0.70	0.27	2.80	0.79
11.	0.39	0.19	0.96	0.47	1.30	1.30
12.	0.40	2.10	0.98	0.59	1.10	1.49
13.	0.67	1.15	2.03	0.68	0.95	1.93
14.	0.72	1.14	2.05	0.74	0.98	2.00
15.	0.79	1.13	2.11	0.80	0.93	2.02
16.	0.80	1.13	2.11	0.82	0.93	2.03

Sl. No.	Values at 30 °C			Values at 50 °C		
	$\bar{X}_{Sr}$	f_{Sr}	f_H	$\bar{X}_{Sr}$	f_{Sr}	f_H
			Sr^{2+}-H^+			
1.	0.04	5.36	0.93	0.05	3.07	0.91
2.	0.11	3.08	0.98	0.12	2.39	0.91
3.	0.15	2.31	1.03	0.13	1.75	0.96
4.	0.24	3.21	0.86	0.19	1.78	0.96
5.	0.24	3.21	0.86	0.24	1.78	0.96
6.	0.24	3.21	0.86	0.28	3.10	0.80
7.	0.25	4.79	0.81	0.28	3.54	0.76
8.	0.26	5.59	0.77	0.29	4.04	0.72
9.	0.27	6.34	0.78	0.30	3.22	0.79
10.	0.27	6.34	0.78	0.33	4.11	0.72
11.	0.47	3.61	1.06	0.51	2.31	1.08
12.	0.57	3.38	1.09	0.60	2.29	1.09
13.	0.65	3.18	1.20	0.67	2.20	1.10
14.	0.72	2.95	1.37	0.74	2.17	1.14
15.	0.77	3.11	1.18	0.78	2.23	1.07
16.	0.78	3.31	0.69	0.80	2.94	0.65

TABLE V

Values of the excess free energies, enthalpies and entropies of mixing for the Ba^{2+}-H^+ *exchange on zironium(IV) phosphosilicate at* 30 *and* 50 °C

Sl. No.	$\bar{X}_{Ba}$	ΔG_m^{ex} (KJ mol^{-1})	ΔH_m^{ex} (KJ mol^{-1})	ΔS_m^{ex} (KJ mol^{-1} degree^{-1})
		At 30 °C		
1.	0.04	0.04	+0.14	0.00
2.	0.09	0.07	−0.04	0.00
3.	0.16	0.14	+0.35	0.00
4.	0.16	0.14	+0.35	0.00
5.	0.21	0.18	0.36	0.00
6.	0.22	0.20	+0.09	0.00
7.	0.23	0.25	+0.15	0.00
8.	0.24	0.27	+0.52	0.00
9.	0.24	0.28	+0.55	0.00
10.	0.25	0.31	+1.70	0.00
11.	0.39	0.71	+0.88	0.00
12.	0.40	0.73	+4.94	+0.01
13.	0.67	0.81	+5.98	+0.02
14.	0.72	0.75	+6.98	0.02
15.	0.79	0.64	+5.95	+0.02
16.	0.80	0.63	+6.35	+0.02
		At 50 °C		
1.	0.07	0.05	−0.63	0.00
2.	0.12	0.10	−0.31	0.00
3.	0.15	0.07	+0.42	0.00
4.	0.15	0.12	+0.40	0.00
5.	0.20	0.19	−0.28	0.00
6.	0.22	0.22	+0.09	0.00
7.	0.23	0.23	−0.41	0.00
8.	0.26	0.31	+0.74	0.00
9.	0.26	0.18	+0.76	0.00
10.	0.27	0.27	+2.03	+0.01
11.	0.47	0.70	+3.83	+0.01
12.	0.59	0.59	+9.24	+0.03
13.	0.68	0.47	+6.39	+0.02
14.	0.74	0.27	+8.05	+0.02
15.	0.80	0.25	+6.80	+0.02
16.	0.82	0.19	+7.33	+0.02

temperature. A comparison of the selectivity coefficients for the Ba^{2+}-H^+ and Sr^{2+}-H^+ exchanges shows that the material is more selective for Ba^{2+} ions.

The standard enthalpy changes, $\Delta H°$, were in accordance with the temperature dependent exchanges and reactions being endothermic for both the systems. The

lower values of Ba^{2+}-H^+ exchanges than the Sr^{2+}-H^+ exchanges confirm the above conclusion. A gain in standard entropy changes ($\Delta S°$) for both exchanges reveals their endothermic behaviour.

The deviation of activity coefficients from unity (Tables IV & V) indicates a heterogeneous distribution of ions at the ZPS surface. Also, the values are high, a characteristic shown earlier[16,9] by solid phases in case of ions with unlike charges interacting on non-ideal surfaces.

TABLE VI

Values of the excess free energies, enthalpies and entropies of mixing for the Sr^{2+}-H^+ *exchange on zirconium(IV) phosphosilicate at* 30 *and* 50 °C

Sl. No.	Xs_r	G^E_m (KJ mol^{-1})	H^E_m (KJ mol^{-1})	S^E_m (KJ mol^{-1} degree^{-1})
		At 30 °C		
1.	0.04	0.01	1.81	0.01
2.	0.11	0.25	3.39	0.01
3.	0.15	0.38	3.91	0.01
4.	0.24	0.40	2.19	0.01
5.	0.24	0.41	2.28	0.01
6.	0.24	0.41	0.50	0.01
7.	0.25	0.57	4.90	0.01
8.	0.26	0.66	5.26	0.02
9.	0.27	0.82	6.64	0.02
10.	0.27	0.82	6.95	0.02
11.	0.47	1.60	7.68	0 02
12.	0.57	1.82	8.32	0.02
13.	0.65	2.05	7.83	0.02
14.	0.72	2.17	10.30	0.02
15.	0.77	2.30	10.71	0.03
16.	0.78	2.33	11.18	0.03
		At 50 °C		
1.	0.05	0.02	2.37	0.00
2.	0.12	0.07	3.97	0.01
3.	0.13	0.23	3.98	0.01
4.	0.19	0.29	1.23	0.00
5.	0.24	0.28	2.73	0.00
6.	0.26	0.35	2.79	0.00
7.	0.28	0.43	5.92	0.02
8.	0.29	0.44	6.23	0.02
9.	0.30	0.64	8.34	0.02
10.	0.33	0.63	8.67	0.02
11.	0.51	1.38	9.66	0.03
12.	0.60	1.43	10.02	0.02
13.	0.67	1.51	9.34	0.03
14.	0.74	1.63	11.81	0.03
15.	0.78	1.72	12.32	0.03
16.	0.80	1.78	12.55	0.03

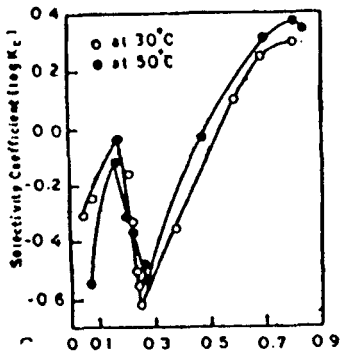


FIG 3 Plots of log K_c *Vs.* $\bar{\nu}M$ on *ZPS* for Ba^{2+}-H^+ at 30 and 50 °C

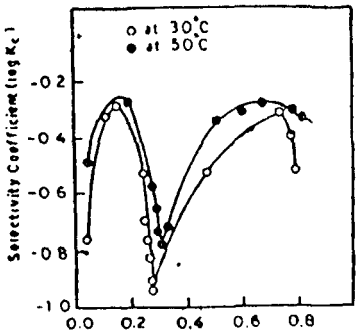


FIG 4 Plots of log K_c *Vs.* $\bar{\nu}M$ on *ZPS* for Sr^{2+}-H^+ at 30 and 50 °C

To further examine the deviation of these heterogeneous systems from an ideal situation, the excess thermodynamic functions were calculated using the equations 9, 10 & 11. Table VI summarises the values. The excess free energy values are positive and increase with the concentration of Ba^{2+} and Sr^{2+} ions. The values of excess enthalpy and entropy changes are in accordance with the observations of Vansant and Utterhoeven,[13] Gast and Klobe,[14] Howery and Thomas[12] on clays.

ACKNOWLEDGEMENT

The authors are grateful to Professor M Qureshi for providing research facilities and to the C.S.I.R. (India) for the financial assistance to one of them (U.S.).

REFERENCES

1. H F Walton *Anal Chem* 52 (1980) 15R
2. L Baetsle *J inorg nucl Chem* 25 (1963) 271
3. G H Nancollas and B V K S R A Tilak *J inorg nucl Chem* 31 (1969) 3643
4. G Alberti and U Costantino *J inorg nucl Chem* 36 (1974) 653
5. J P Rawat and P S Thind *J Indian Chem Soc* 57 (1980) 819
6. J P Rawat and K P S Muktawat *J inorg nucl Chem* 43 (1981) 2121
7. K G Varshney R P Singh and S Rani *Acta Chim Hung* 115 (1984) 403
8. R M S Ramaswamy B L Jangida and M Sundaresan *Proc. Ion-Exchange Symp* (1978) 187
9. R A Robinson and R H Stokes *Trans Faraday Soc* 45 (1949) 612
10. J P Singhal and R P Singh *Acta Chim Hung* 93 (1977) 307
11. S Glasstone *Text Book of Physical Chemistry* Mac Milian and Company Ltd. London (1960) 827
12. D G Howery and H C Thomas *J phys Chem* 69 (1965) 531
13. E F Vansant and Utterhoeven *Clays and Clay Min* 20 (1972) 47
14. R G Gast and W D Klobe *Clays and Clay Min* 19 (1971) 311
15. J P Singhal and R P Singh *J Soil Sci* 24 (1973) 271
16. J P Singhal R P Singh and D Kumar *J Indian Chem Soc* 52 (1975) 380

Colloids and Surfaces, 16 (1985) 207—218
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

4·5

THERMODYNAMICS OF THE Ca(II)—H(I) AND Mg(II)—H(I) EXCHANGES ON ZIRCONIUM(IV) PHOSPHOSILICATE CATION-EXCHANGER

KRISHNA GOPAL VARSHNEY[1,*], RISHI PAL SINGH[2] and UMA SHARMA[1]

[1]*Analytical Laboratories, Chemistry Section, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202001 (India)*
[2]*Section of Plant Pathology and Nematology, Department of Botany, Aligarh Muslim University, Aligarh-202001 (India)*

(Received 31 October 1984; accepted in final form 18 June 1985)

ABSTRACT

The equilibrium exchange of Ca(II) and Mg(II) ions with the hydrogen form of zirconium(IV) phosphosilicate has been studied at 30 and 50°C. On the basis of the exchange isotherms, various thermodynamic parameters have been calculated and some predictions made for the exchange processes taking place in the material. The surface phase activity coefficients have also been evaluated, which give the excess free energies (ΔG_m^x), enthalpies (ΔH_m^x) and entropies (ΔS_m^x) of mixing.

INTRODUCTION

Inorganic ion-exchangers are in general more resistant to heat and gamma radiation than organic resins. Also, they swell to a negligible extent in water due to their rigid matrices, thus representing a simple system for a thermodynamic study. However, only zirconium(IV) phosphate has received considerable attention in this regard [1—4]. Only a few studies have reported on the thermodynamics of the ion-exchange behaviour of other materials of this class [5—8]. In continuation of our efforts [9], the present article summarizes the results of a thermodynamic study of the exchange of Ca(II) and Mg(II) ions with H(I) ions on zirconium(IV) phosphosilicate (ZPS).

MATERIALS AND METHODS

Reagents and chemicals

Zirconyl chloride and sodium silicate were BDH (Poole, United Kingdom) and Reidel (DEHAENAG, Seelze Hannover, F.R.G.) products, respectively. All other reagents and chemicals were of AnalaR grade.

*Author for all correspondence.

0166-6622/85/$03.30

Apparatus

A waterbath incubator shaker having a temperature variation of ± 0.5°C was used for the equilibrium studies.

Synthesis of the ion-exchanger

To an aqueous solution of sodium silicate (1000 ml, 0.1 mol dm^{-3}) were added conc. HCl (50 ml) and an aqueous zirconium oxychloride solution (1000 ml, 0.1 ml dm^{-3}). The pH of the mixture was kept at 9—10 by the addition of NH_4OH, and the resultant slurry was allowed to stand overnight, filtered, washed with demineralized water (DMW) and mixed with a H_3PO_4–HNO_3 mixture (total 1000 ml, 1 mol dm^{-3} each). The gel thus obtained was kept overnight, filtered, washed thoroughly with DMW, dried at 45°C in an air oven and placed in DMW where it formed small granules which were converted into the H(I) form by treating with 1 mol dm^{-3} HNO_3. The Na-ion exchange capacity of cation-exchanger (ZPS) was found to be 2.19 meq per dry g.

Equilibrium experiments

Samples (0.2 g) of the exchanger were shaken in stoppered conical flasks at the desired temperatures (30 and 50°C) for 12 h, with the 20-ml fractions of the metal-ion solution having a constant ionic strength (0.03 *M*). The supernatant liquid was analyzed for the metal and hydrogen ions, respectively.

RESULTS AND DISCUSSION

The ion-exchange process occurring on the ZPS surface can be represented by the equation:

$$2(H^+ - ZPS) + M^{2+} \rightleftharpoons M^{2+}(ZPS)_2 + 2H^+ \quad (1)$$

where M^{2+} represents the Ca(II) and Mg(II) ions. This equation can also be written as

$$\bar{C}_M + C_H \rightleftharpoons \bar{C}_H + C_M \quad (2)$$

where the barred and unbarred quantities represent the equivalent concentrations in the exchanger and solution phases, respectively. The equivalent ionic fractions of the counter-ions in the ZPS and solution phases ($\bar{X}_M$, $\bar{X}_H$, X_M and X_H) were calculated from the expressions:

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}}, \; X_M = \frac{C_M}{C}, \; \bar{X}_H = \frac{\bar{C}_H}{\bar{C}}, \; X_H = \frac{C_H}{C}$$

where $\bar{C}$ and C are the total electrolyte concentrations in the solid and solution phases, respectively ($\bar{C} = \bar{C}_M + \bar{C}_H$ and $C = C_M + C_H$).

The separation factors were calculated using the relation

$$\alpha_H^M = \frac{\bar{X}_M}{\bar{X}_H} \cdot \frac{X_H}{X_M} \quad (3)$$

TABLE 1

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 30 and 50°C for the Ca(II)—H(I) exchange on zirconium(IV) phosphosilicate

Sample No	$\bar{X}_{Ca}$	X_{Ca}	$\bar{X}_H$	X_H	α_H^{Ca}	K_c	log K_c
30°C							
1	0 03	0 20	0 97	0 86	0 12	0 10	0 99
2	0 07	0 31	0 93	0 86	0 19	0 16	0 79
3	0 15	0 32	0 85	0 89	0 39	0 31	0 51
4	0 19	0 39	0 81	0 68	0 41	0 34	-0 47
5	0 25	0 41	0 75	0 59	0 50	0 39	0 41
6	0 27	0 44	0 73	0 56	0 47	0 36	0 44
7	0 29	0 51	0 71	0 49	0 39	0 27	- 0 57
8	0 29	0 55	0 71	0 45	0 33	0 21	0 68
9	0 29	0 59	0 71	0 41	0 29	0 17	0 77
10	0 30	0 62	0 70	0 38	0 26	0 14	- 0 85
11	0 30	0 68	0 70	0 33	0 22	0 10	0 99
12	0 59	0 68	0 41	0 32	0 34	0 45	0 35
13	0 68	0 71	0 32	0 30	0 80	0 83	- 0 08
14	0 73	0 75	0 27	0 25	0 93	0 88	−0 06
15	0 80	0 80	0 20	0 20	1 03	1 05	-0 02
16	0 81	0 83	0 19	0 17	0 91	0 84	0 08
50°C							
1	0 07	0 13	0 93	0 87	0 45	0 42	0 38
2	0 10	0 28	0 90	0 72	0 28	0 22	- 0 65
3	0 18	0 25	0 82	0 71	0 54	0 47	-0 33
4	0 21	0 37	0 79	0 63	0 46	0 37	0 14
5	0 27	0 35	0 73	0 62	0 62	0 53	0 28
6	0 28	0 45	0 72	0 55	0 47	0 36	0 44
7	0 31	0 49	0 69	0 51	0 47	0 34	−0 49
8	0 32	0 52	0 68	0 48	0 45	0 32	−0 50
9	0 33	0 56	0 67	0 44	0 39	0 25	0 60
10	0 34	0 60	0 66	0 40	0 34	0 21	0 68
11	0 43	0 62	0 57	0 38	0 45	0 30	0 52
12	0 60	0 67	0 40	0 34	0 73	0 60	0 22
13	0 71	0 67	0 29	0 33	1 21	1 38	−0 14
14	0 77	0 71	0 23	0 29	1 32	1 61	0 21
15	0 82	0 78	0 18	0 22	1 26	1 51	0 18
16	0 83	0 82	0 17	0 18	1 26	1 11	0 05

TABLE 2

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 30 and 50°C for Mg(II)—H(I) exchange on zirconium(IV) phosphosilicate

Sample No	$\bar{X}_{Mg}$	X_{Mg}	$\bar{X}_H$	X_H	α_H^{Mg}	K_c	log K_c
30°C							
1	0 06	0 05	0 94	0 95	0 97	0 97	0 01
2	0 09	0 14	0 91	0 86	0 65	0 62	−0 21
3	0 13	0 20	0 87	0 80	0 63	0 59	−0 23
4	0 14	0 33	0 86	0 67	0 27	0 25	- 0 61
5	0 18	0 35	0 82	0 65	0 41	0 32	−0 49
6	0 19	0 41	0 81	0 99	0 33	0 24	−0 62
7	0 21	0 44	0 89	0 56	0 34	0 24	−0 61
8	0 23	0 47	0 77	0 53	0 32	0 22	−0 67
9	0 23	0 53	0 77	0 48	0 27	0 16	−0 79
10	0 23	0 56	0 77	0 44	0 24	0 14	−0 86
11	0 44	0 56	0 56	0 44	0 62	0 49	−0 31
12	0 54	0 65	0 46	0 35	0 65	0 50	−0 30
13	0 64	0 67	0 36	0 33	0 87	0 80	−0 10
14	0 66	0 75	0 34	0 25	0 66	0 49	- 0 31
15	0 70	0 83	0 30	0 17	0 50	0 29	0 54
16	0 71	0 85	0 29	0 15	0 42	0 21	−0 68
50°C							
1	0 06	0 02	0 92	0 98	1 07	1 20	+0 08
2	0 10	0 11	0 90	0 79	0 89	0 88	0 06
3	0 14	0 16	0 86	0 85	0 89	0 87	0 32
4	0 17	0 27	0 83	0 73	0 55	0 48	−0 44
5	0 19	0 34	0 81	0 66	0 45	0 37	0 53
6	0 21	0 38	0 79	0 62	0 45	0 36	−0 59
7	0 23	0 43	0 77	0 57	0 40	0 29	- 0 54
8	0 24	0 47	0 76	0 53	0 36	0 26	−0 57
9	0 27	0 47	0 73	0 53	0 41	0 29	0 08
10	0 27	0 52	0 73	0 48	0 39	0 27	−0 04
11	0 49	0 49	0 51	0 51	0 88	0 83	−0 17
12	0 59	0 58	0 41	0 62	0 84	1 10	−0 06
13	0 64	0 69	0 36	0 31	0 53	0 67	−0 39
14	0 70	0 71	0 30	0 29	0 53	0 88	−0 06
15	0 73	0 81	0 27	0 19	0 61	0 41	-0 39
16	0 74	0 84	0 26	0 16	0 12	0 35	−0 46

Since the solutions were taken in the dilute range of concentrations, the selectivity coefficients were calculated from the expression

$$K_c = \frac{\bar{X}_M}{(\bar{X}_H)^2} \cdot \frac{(X_H)^2}{X_M} \qquad (4)$$

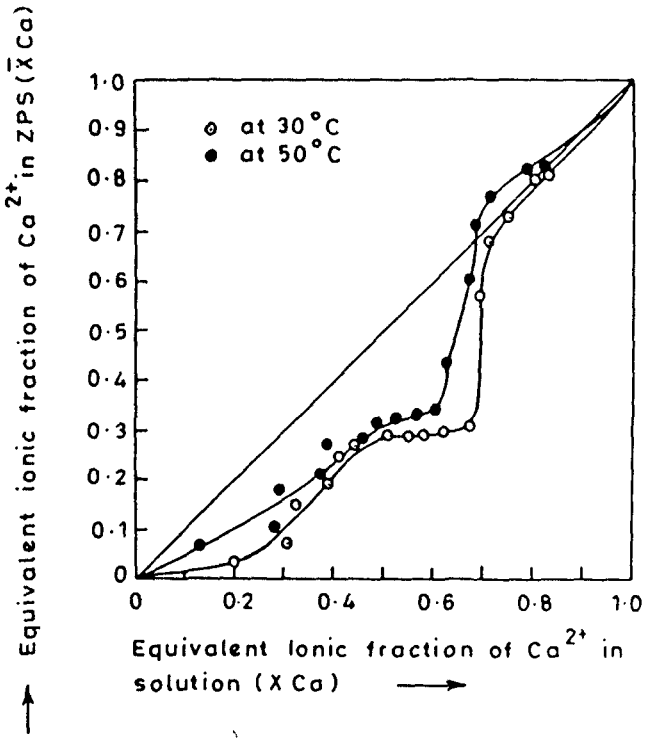


Fig. 1. Ion-exchange isotherm of Ca(II)–H(I) exchange on zirconium(IV) phosphosilicate.

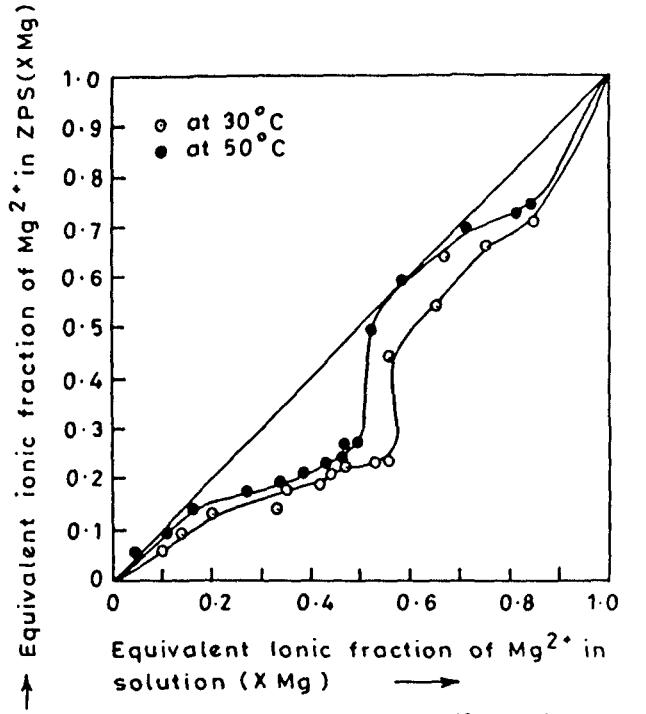


Fig. 2. Ion-exchange isotherm of Mg(II)–H(I) exchange on zirconium(IV) phosphosilicate.

The various values obtained at 30 and 50°C are summarized in Tables 1 and 2, and the exchange isotherms are shown in Figs 1 and 2. These values indicate a greater preference of the exchanger, in general, for H(I) ions compared with the Ca(II) and Mg(II) ions, except in the X_{Ca} range 0.65–0.85 (Fig. 1), where the exchanger shows a preference for Ca(II) ions at 50°C. Also, there is a marked increase in the adsorption of metal ions in a specified ionic fraction range — from 0.5 to 0.7 for X_{Ca}, and from 0.5 to 0.6 for X_{Mg}.

The selectivity coefficients (K_c) obtained from Eqn (4) are summarized in Tables 1 and 2 and their variation with $\bar{X}_M$ is shown in Figs 3 and 4. The thermodynamic equilibrium constants (K) were obtained from the relation [10]:

$$\ln K = -(Z_A - Z_B) - \int_0^1 \ln K_c \, d\bar{X}_M \qquad (5)$$

where Z_A and Z_B are the valencies of the competing ions. The integrals were

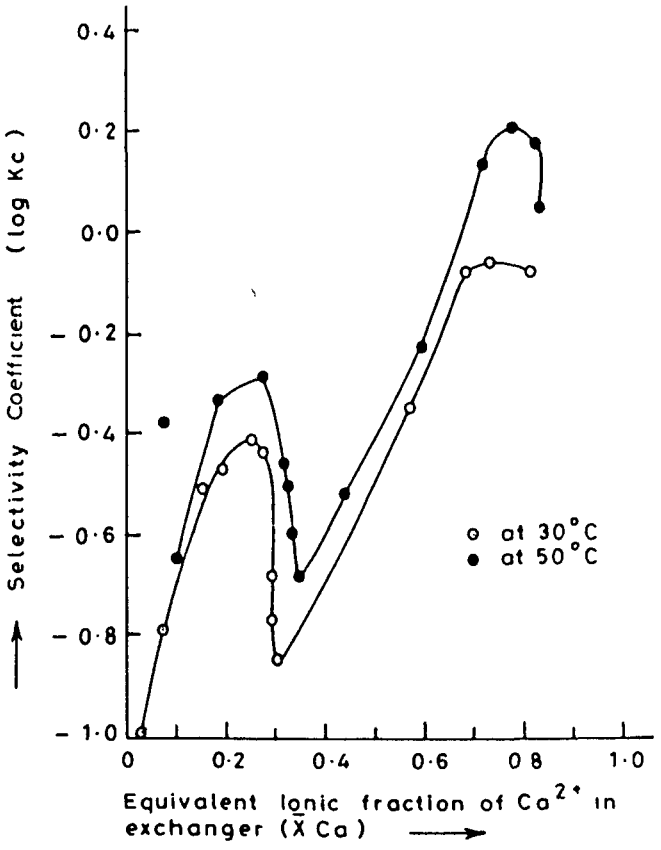


Fig. 3. Logarithm of selectivity coefficient versus ionic fraction of Ca(II) in H(I) form exchanger.

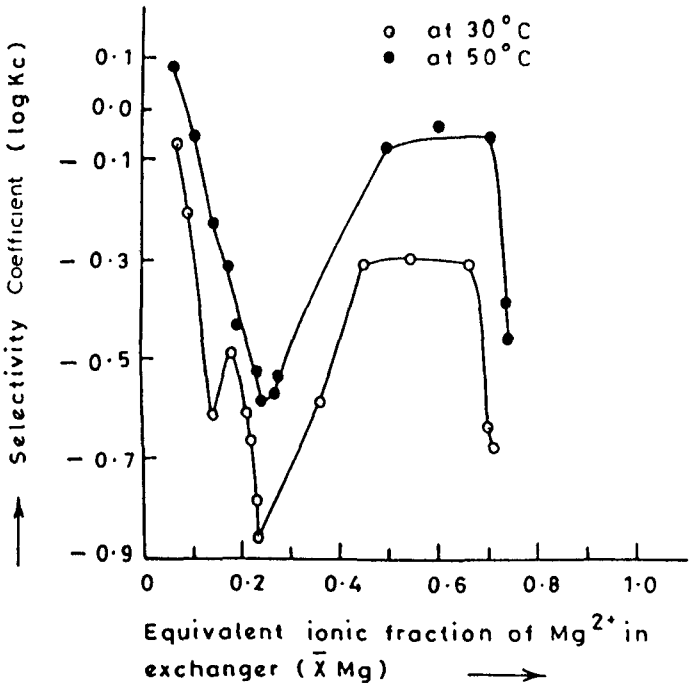


Fig. 4. Logarithm of selectivity coefficient versus ionic fraction of Mg(II) in H(I) form exchanger.

evaluated from the areas under the curves of Figs 3 and 4 using the trapezoidal rule [11] and the K values are summarized in Table 3. In both the exchanges the K value is lower at 50°C than at 30°C, indicating a lower preference for Ca(II) and Mg(II) ions at a higher temperature. These results are in accordance with the exchange isotherms. On comparing the exchange behaviour of ZPS for Ca(II) and Mg(II) ions, it is observed that the K value is higher for the Ca(II)—H(I) exchange process. The positive standard free energy (ΔG^0) values [12] for the interactions at both temperatures indicate that ZPS has a lower

TABLE 3

Thermodynamic values for the Ca(II)—H(I) and Mg(II)—H(I) exchanges on zirconium(IV) phosphosilicate at 30 and 50°C

Thermodynamic parameters	Values in Ca(II)—H(I) system		Values in Mg(II)—H(I) system	
	30°C	50°C	30°C	50°C
K	0.87	0.58	0.71	0 50
ΔG° (KJ mol^{-1})	0.36	1.45	0.87	1 86
ΔH° (KJ mol^{-1})	−16.12		−14.17	
ΔS° (KJ mol^{-1} degree^{-1})	−0.054	−0.054	−0.049	0.049

TABLE 4

Values of the activity coefficients for the different Ca(II)—H(I) and Mg(II)—H(I) exchanges on zirconium(IV) phosphosilicate at 30 and 50°C

Sample No.	Ca(II)—H(I)					
	Values at 30°C			Values at 50°C		
	$\bar{X}_{Ca}$	f_{Ca}	f_H	$\bar{X}_{Ca}$	f_{Ca}	f_H
1	0.03	8.73	0.96	0.07	2.49	0.91
2	0.07	6.16	0.95	0.10	2.35	0.93
3	0.15	0.38	1.00	0.18	2.13	0.95
4	0.19	3.01	1.02	0.21	1.97	0.97
5	0.25	2.78	1.03	0.27	1.88	0.96
6	0.27	2.73	0.97	0.28	2.24	0.79
7	0.29	5.31	0.90	0.31	2.56	0.87
8	0.29	5.31	0.90	0.32	2.68	0.85
9	0.29	5.31	0.90	0.33	3.13	0.77
10	0.30	6.04	0.85	0.34	3.43	0.75
11	0.30	5.86	0.87	0.43	0.86	1.21
12	0.57	3.09	1.38	0.60	2.00	1.21
13	0.68	2.48	2.02	0.71	1.54	1.99
14	0.73	2.40	2.19	0.72	1.45	2.30
15	0.80	2.43	2.07	0.82	1.47	2.08
16	0.81	2.44	2.03	0.83	1.55	1.74

Sample No.	Mg(II)—H(I)					
	Values at 30°C			Values at 50°C		
	$\bar{X}_{Mg}$	f_{Mg}	f_H	$\bar{X}_{Mg}$	f_{Mg}	f_H
1	0.06	1.30	0.99	0.06	1.11	1.12
2	0.09	1.75	0.96	0.10	1.37	0.93
3	0.13	3.16	0.81	0.15	1.96	0.92
4	0.14	3.49	0.88	0.17	2.43	0.88
5	0.18	2.88	0.91	0.19	1.89	0.88
6	0.19	3.66	0.88	0.22	2.90	0.88
7	0.21	3.54	0.87	0.23	3.22	0.86
8	0.23	3.94	0.84	0.24	3.22	0.85
9	0.23	5.44	0.77	0.27	1.48	1.12
10	0.23	2.35	0.77	0.27	1.48	1.12
11	0.44	2.31	1.15	0.45	1.31	1.20
12	0.54	2.29	1.16	0.59	1.50	1.01
13	0.64	2.36	1.11	0.64	1.48	1.03
14	0.66	2.76	1.11	0.70	1.50	0.99
15	0.70	2.76	0.80	0.73	1.73	1.42
16	0.71	3.03	0.63	0.74	1.79	0.62

preference for Ca(II) and Mg(II) than for H(I). Hence, the replacement of H(I) by Ca(II) or Mg(II) is not spontaneous. It is in accordance with the inference drawn from the exchange isotherms. The reaction was accompanied by a negative enthalpy change in both cases. It is presumably due to the smaller hydrated ionic radii and higher charge of Ca(II) and Mg(II) ions compared with H(I). It also suggests that the adsorption of Ca(II) and Mg(II) ions decreases with the rise in temperature. The exchange process is also

TABLE 5

Values of the excess free energies, enthalpies and entropies mixing for the Ca(II)–H(I) exchange on zirconium(IV) phosphosilicate at 30 and 50°C

Sample No.	$\bar{X}_{Ca}$	ΔG_m^x (KJ mol^{-1})	ΔH_m^x (KJ mol^{-1})	ΔS_m^x (KJ mol^{-1} degrees^{-1})
30°C				
1	0.03	0.04	0.03	0.01
2	0.07	0.21	3.43	0.01
3	0.15	0.47	4.35	0.01
4	0.19	0.59	4.20	0.01
5	0.25	0.76	5.60	0.02
6	0.27	1.09	14.51	0.04
7	0.29	1.02	9.11	0.03
8	0.29	1.04	9.26	0.03
9	0.29	1.04	10.20	0.03
10	0.30	1.09	9.96	0.03
11	0.30	1.11	13.44	0.04
12	0.59	1.96	11.63	0 03
13	0.68	2.13	12.60	0.03
14	0.73	2.15	13.63	0.04
15	0.80	2.16	15.19	0.04
16	0.81	2.16	15.12	0.04
50°C				
1	0.07	−0.07	5.47	0.12
2	0.10	−0.05	5.03	0.02
3	0.18	0.25	5.41	0.02
4	0.21	0.31	5.05	0.01
5	0.27	0.38	6.58	0.02
6	0.28	0.16	16.75	0.05
7	0.31	0.50	10.90	0.03
8	0.32	0.56	11.44	0.03
9	0.33	0.53	12.21	0.04
10	0.34	0.62	12.03	0.04
11	0.43	0.12	27.74	0.08
12	0.60	1.31	13.59	0.04
13	0.71	1.36	14.95	0.04
14	0.77	1.29	16.29	0.05
15	0.82	1.21	17.61	0.05
16	0.83	1.23	17.35	0.05

TABLE 6

Values of the excess free energies, enthalpies and entropies of mixing for the Mg(II)—H(I) exchange on zirconium(IV) phosphosilicate at 30 and 50°C

Sample No	X_{Mg}	ΔG_m^x (KJ mol $^{-1}$)	ΔH_m^x (KJ mol $^{-1}$)	ΔS_m^x (KJ mol $^{-1}$ degree $^{-1}$)
30°C				
1	0 06	0 00	−4 28	−0 01
2	0 09	0 04	2 02	0 01
3	0 13	−0 08	0 80	0 01
4	0 14	0 14	1 70	0 01
5	0 18	0 28	3 77	0 01
6	0 19	0 35	2 40	0 01
7	0 21	0 40	1 57	0 00
8	0 23	0 43	1 61	0 00
9	0 23	0 45	1 19	0 00
10	0 23	0 47	0 41	0 00
11	0 44	1 15	8 99	0 03
12	0 54	1 30	11 25	0 03
13	0 64	1 47	12 14	0 04
14	0 66	1 52	12 90	0 04
15	0 70	1 62	5 92	0 01
16	0 71	1 64	14 45	0 04
50°C				
1	0 06	0 30	−4 78	−0 02
2	0 10	−0 09	2 36	0 01
3	0 14	0 26	−1 76	−0 01
4	0 17	0 12	2 38	0 01
5	0 19	0 05	4 47	0 01
6	0 21	0 29	2 96	0 01
7	0 23	0 36	1 83	0 00
8	0 24	0 41	2 03	0 01
9	0 27	0 50	3 10	0 01
10	0 27	0 50	3 40	0 01
11	0 49	0 60	11 43	0 03
12	0 59	0 65	13 43	0 04
13	0 64	0 70	13 69	0 04
14	0 70	0 75	15 14	0 04
15	0 73	1 32	7 80	0 02
16	0 74	0 83	17 15	0 05

governed by the entropy change. A negative entropy change for both the exchanges means a preference for H(I) ions by the exchanger It appears that, in these systems, the hydration shells around Ca(II) and Mg(II) ions remain intact during their adsorption, thus contributing to a greater order of the system.

The activity coefficients (f_M and f_H) were calculated from the following expressions [13, 14]:

$$\ln f_M = (\bar{X}_M - 1) \ln K_c - \int_0^{\bar{X}_M} \ln K_c \, d\bar{X}_M \quad (6)$$

$$\ln f_H = \bar{X}_M \ln K_c - \int_0^{\bar{X}_M} \ln K_c \, d\bar{X}_M \quad (7)$$

The deviation of activity coefficients from unity (Table 4) indicates a heterogeneous distribution of ions at the ZPS surface. Also, the values are high, a characteristic shown earlier [15] by solid phases in the case of ions with different charges interacting on non-ideal surfaces.

To examine further the deviation of these heterogeneous systems from ideality, the excess thermodynamic functions for these systems were calculated from the expressions [16, 17]:

$$\Delta G_m^x = RT[\bar{X}_M \ln f_M + \bar{X}_H \ln f_H] \quad (8)$$

$$\Delta H_m^x = -RT^2 \left[\bar{X}_M \left(\frac{\ln f_M}{T}\right) + \bar{X}_H \left(\frac{\ln f_H}{T}\right)\right] \quad (9)$$

and

$$\Delta G_m^x = H_m^x - T\Delta S_m^x \quad (10)$$

where ΔG_m^x, ΔH_m^x and ΔS_m^x are the excess free energies, enthalpies and entropies of mixing, respectively. The excess free energy values are positive (Tables 5 and 6) and increase with the excess enthalpy and entropy changes in accordance with the observations on clays [14, 16].

ACKNOWLEDGEMENTS

The authors thank Dr K.T. Nasim for research facilities and the C.S.I.R. (India) for the financial assistance.

REFERENCES

1 E.M. Larsen and D.R. Vissers, J. Phys. Chem., 64 (1960) 1732.
2 L.H. Baetsle, J. Inorg. Nucl. Chem., 25 (1963) 271.
3 G.H. Nancollas and B.V.K.S.R.A. Tilak, J. Inorg. Nucl. Chem., 31 (1969) 3643.
4 G. Alberti and U. Costantino, J. Inorg. Nucl. Chem., 36 (1974) 653.
5 J.P. Rawat and D.K. Singh, Anal. Chim. Acta, 87 (1976) 157.
6 J.P. Rawat and K.P.S. Muktawat, J. Inorg. Nucl. Chem., 43 (1981) 2121.
7 K.G. Varshney, R.P. Singh and S. Rani, Acta Chim. Acad. Sci. Hung., 115 (1984) 403.
8 K.G. Varshney, R.P. Singh and S. Rani, Proc. Ind. Nat. Sci. Acad. Part A, 50 (1984) 75.
9 K.G. Varshney, R.P. Singh and U. Sharma, Proc. Ind. Nat. Sci. Acad., in press.
10 G.L. Gains and H.C. Thomas, J. Chem. Phys., 21 (1953) 714.
11 J.P. Singhal and R.P. Singh, Acta. Chim. Acad. Sci. Hung., 93 (1977) 307.
12 S. Glasstone, Text Book of Physical Chemistry, Macmillan and Co. Ltd., London, 1960, p. 827.

13 M.H. El-Sayed, R.G. Burau and K.L. Babcock, Soil Sci. Soc. Am. Proc., 34 (1970) 397.
14 D.G. Howery and H.C. Thomas, J. Phys. Chem., 69 (1965) 531.
15 J. Diest and O. Talibuddeen, J. Soil Sci., 18 (1967) 125.
16 R.G. Gast and W.D. Klobe, Clays Clay Miner., 19 (1971) 311.
17 A.P. Vanselow, Soil Sci., 33 (1932) 95